1980

Effect of Capillary Diameter on the Rate of Radiation Induced Polymerization of Acrylamide in Saline Solutions Containing Dissolved Phosphorus-32.

Satyajit Verma
Louisiana State University and Agricultural & Mechanical College

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EFFECT OF CAPILLARY DIAMETER ON THE RATE OF RADIATION INDUCED POLYMERIZATION OF ACRYLAMIDE IN SALINE SOLUTIONS CONTAINING DISSOLVED PHOSPHORUS-32

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EFFECT OF CAPILLARY DIAMETER ON THE RATE
OF RADIATION INDUCED POLYMERIZATION OF ACRYLAMIDE
IN SALINE SOLUTIONS CONTAINING DISSOLVED $^{32}$P

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Department of Chemical Engineering

by

Satyajit Verma
B. Tech. Indian Institute of Technology, Kanpur, India, 1974
M.S. Louisiana State University, 1976

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ABSTRACT

Radiation induced solution polymerization of acrylamide was studied at 80°C in tubes with diameters of 6, 2.29, 0.89 and 0.38 mm. The tubes were filled with aqueous solutions of 3% acrylamide, 10% NaCl and sufficient neutralized orthophosphoric acid to produce a specific radioactivity of 1 mCi/ml. of dissolved $^{32}$P. Distinctly higher initial rates of increase of solution viscosity were observed with increasing tube diameter. Kinetic studies were done also with 3% acrylamide in 0, 5 and 10% salt solutions at 81.5°C and 28°C; the reaction induced by external irradiation from $^{60}$Co. Other systems studied were 1 and 1.5% acrylamide in 0, 5 and 10% salt and 2% acrylamide at 28°C also under $^{60}$Co. The solutions at higher temperatures initially increased in viscosity and then degraded as irradiation continued. No significant decrease in the solution viscosities with reaction time was observed in the solution polymerization of acrylamide initiated with $K_2S_2O_8$ at 80°C, although the presence of salt reduced the maximum viscosity attained. The viscosities of the solutions irradiated at 28°C first increased with the absorbed dose, then stayed constant or decreased
slightly, and if the initial monomer concentration were above a critical value, i.e. 1.5 w/v %, finally cross-linked. Pseudo-phase separation was observed during polymerization; the polymer tended to accumulate in the bottom phase. The presence of salt increased the rate of reaction and reduced the total dose needed for cross-linking. The relative viscosity vs. dose curves at 28°C for different salt contents coincided when plotted as relative viscosity vs. conversion. Solutions of polyacrylamide (0.2, 0.4, 0.6 and 1.0% in water and 0.1, 0.5 and 1.0% in 10% saline water) were also irradiated at 28°C with $^{60}\text{Co}$. A rapid decrease in viscosity of the samples was observed prior to gelation. The presence of salt delayed gelation.

An expression for the extent of reaction as a function of dose (or time) and the size of the capillary containing the radioactive fluid was derived from the energy transfer characteristics of $\beta$ particles. It was also shown that conversion ($x$) vs. time ($t$) data for reactions in viscous media may be linearized on a $-\ln(1-x)$ vs. $\ln t$ plot. The applicability of the diameter dependence of reaction rate to selectively plug large channels in oil reservoirs was briefly discussed.
I. INTRODUCTION

With the spiraling cost of oil throughout the world, much concern has been generated over the amount of crude oil left behind in the oil reservoirs after the completion of primary recovery. Extensive research work is being carried on in both industries and universities to evaluate and improve the efficiency of oil recovery by techniques of water-, polymer-, surfactant-, CO$_2$-, steam-, caustic-, etc., flooding of the oil reservoirs. The aim is to improve the sweep of the reservoir or to reduce undesirable loss of the pushing fluid. The present work is an academic inquiry into the possibility of using an aqueous solution of a polymerizable monomer for selective plugging of large channels that may exist in oil reservoirs and which, if left unaltered, would cause the pusher fluid to bypass the surrounding oil-bearing rocks.

A. Literature Review

Al. Polyacrylamide in Enhanced Oil Recovery

Poly(acrylamide), as one of the water soluble polymers [1-3], is best known to the present day chemical engineer.
for its flocculating and viscosity enhancing properties. Owing to the fact that its monomer, acrylamide, is easy to polymerize into a high molecular weight polymer and that aqueous solutions of this polymer have high viscosity at low concentrations, polyacrylamide has been a prime candidate for enhanced oil recovery for quite some time. It is a matter of common knowledge, that after the primary recovery, 30-60% of the original crude oil still remains trapped in the reservoir rocks. Water flooding does a poor job of recovering any significant portion of this oil because of the phenomenon of viscous fingering (slippage of water past more viscous oil). It was, however, determined through extensive experimentation that addition of small amounts (typically 200 ppm to 1500 ppm) of polyacrylamide or its partially hydrolyzed counterpart [4-7] not only reduced this slippage but also increased the areal sweep efficiency (fraction of total reservoir swept by the thickened water). Various additives e.g., NH₄OH [8], surfactants [9,10], Na₂CO₃ [11,12], sodium oleate/palmitate and Na₂CO₃/Na₄PO₇ [13] were added to water to stabilize the polymer and/or to decrease the oil-water interfacial tension, leading to increased recovery. As the promise and interest in polymer flooding grew, laboratory and field [14-19] studies were conducted to understand the nature of mobility control [20-23], flow of the polymer solution through porous media [24,25], rheology,
adsorption [26-28], and thermal stability [29], etc., of the polymer solution under reservoir conditions. It was observed that at high temperatures (150°F-300°F), high shear rates (because of flow through fine pores) and in the presence of salts (2-10%) of both monovalent and multivalent ions — conditions that are typical of oil reservoirs [30] — the polymer solution rapidly degraded due to shear [31], lost its viscosity because of the ionic environment [32,33] and was adsorbed [19]. It was also determined that approximately 30% of the pore volume was inaccessible to the polymers [34,35] simply because the adsorbed polymers reduced the effective size of the pores. These results and the prevailing economic conditions discouraged the use of polyacrylamide to improve water flooding, until recently (1974) when the skyrocketing crude oil prices rejuvenated interest in the abandoned oil fields. Recent publications discuss its potential [36,37]; various ongoing and planned projects [38,39]; and comparison of polymer, polymer-micellar and polymer-caustic floods with other methods of enhanced oil recovery (EOR); e.g., CO₂ miscible, steam flooding or in-situ combustion, etc., [38]. One publication [40] discusses the basis for EOR method selection, while another [41] claims improved performance by polymer flooding preceded by a micellar slug. Solution properties of polyacrylamides have also been reported [42] and its performance has been compared with water soluble
polysaccharides [43] which have lower ionic susceptibilities. Other water-soluble polymers suggested to assist in the enhanced oil recovery are mucilage gum derived from flax meal [44], phosphorylated mannan -- an exocellular polysaccharide synthesized from glucose by a yeast [45], xanthan gum and scleroglucan [46], carboxymethylhydroxyethyl cellulose in the presence of \( \text{Cr}^{+3} \) or \( \text{Al}^{+3} \) [47], biopolymer synthesized by an algae [48] and alkali treated effluents from the fermentation of Pseudomonas methanica [49].

It should be mentioned at this point that in order to overcome the high pressure drop requirements and the shear degradation of the polymer as it passed through the well bore, it has been suggested [50,51] that a monomer solution containing a catalyst be injected into the oil bearing formation. In this way the polymer solution was formed some distance away from the well bore after the latent period of the catalyst expired.

The use of polyacrylamide in tertiary oil recovery is not confined to increasing the sweep efficiency or supporting the micellar bank but it extends also to plugging faulty formations in the oil reservoir. The presence of hollow cavities, which cause the pusher fluid to simply bypass the oil rich surroundings, and the so-called thief zones through which the pusher fluid may be lost, never to be recovered, are both undesirable features. The practice so far has been to inject a heat sensitive mixture of
chemicals into the formation, so that a crosslinked gel is formed at the elevated reservoir temperature after a predetermined time and the opening is plugged. Various compositions have been suggested -- notable among these are: partially hydrolyzed polyacrylamide and ethylene glycol [52], microgel of partially hydrolyzed polyacrylamide [53,54], solution of a polysaccharide preceded by Ca$^{+2}$ or Mg$^{+2}$ rich aqueous slug [55], acid catalyzed in-situ polymerization of furfuryl alcohol [56], persulfate initiated polymerization of acrylamide-acrylonitrile mixture with a phenolic ester [57], partially hydrolyzed polyacrylamide, aluminum and citrate ion complex [58], polyacrylamide, Na$_2$Cr$_2$O$_7$ and NaH SO$_3$ [59], carboxymethyl cellulose and polyacrylamide and Na$_2$Cr$_2$O$_7$ + NaH SO$_3$ [60], polyamide beads dispersed in polyacrylamide solution [61], mixture of various water soluble resins [62], lignosulfonate and a mixed activator of Na$_2$Cr$_2$O$_7$ and salt [63,64] and (NH$_4$)$_2$SO$_4$, hydroxethyl cellulose and alkaalimetal silicate [65]. There are a few disadvantages to these mixtures: (1) Most of the chemicals used are very sensitive to the ionic environment, (2) The rate of gelation is a function of the temperature and salt concentration which may vary within the same reservoir. As a result the gelation may occur too soon or too late, and (3) The gel formed will indiscriminately plug up the general area -- large cavities and small pores alike. As a result the oil contained in the fine pores is lost to recovery.
The present work deals with these problems, and specifically the last one. It proposes a method by which only cavities larger than a certain diameter would be plugged with the help of dissolved radioactive material in the pusher fluid. Before presenting the experimental results and their interpretation, it is instructive to look into the polymerization and crosslinking reactions of the monomer-acrylamide.

A2. Chemical Polymerization and Crosslinking of Acrylamide

Acrylamide (H₂C=CH-C-NH₂) is a crystalline solid soluble in water and most organic solvents. It readily polymerizes by conventional free radical methods [66-69] to yield poly-acrylamide

\[ n \text{CH}_2=\text{CH-C-NH}_2 \rightarrow \text{CH}_2=\text{CH} \rightarrow_n \]

which is soluble in water, ethylene glycol and formamide [70]. Anionic polymerization of acrylamide in aromatic solvents under anhydrous conditions leads to a water-insoluble polymer, poly-β-alanine [71,72]:

\[ n \text{CH}_2=\text{CH-C-NH}_2 \rightarrow \text{CH}_2=\text{CH}_2-\text{C-NH}_2 \rightarrow_n \]

Industrially, the most important process of manufacture of polyacrylamide is redox or free radical polymerization in aqueous solutions of 10-30% acrylamide at 30-60°C and a
catalyst concentration of 0.01-1.0% based on the monomer [73-75]. Studies have been reported on the polymerization of acrylamide in redox systems [76-79], peroxide initiator [80,81], under high pressure [82], in the presence of an oxygen carrier [83], surfactants [84], photosensitive initiator [85], ionizing radiation (discussed in the next section), and in the absence of any catalyst [86]. The polymerization follows the familiar course [87]:

**Initiation:**

\[ I \xrightarrow{k_d} 2R^* \]

\[ R^* + M \xrightarrow{k_i} RM^* \quad R_i = 2f k_d[I] \] (1)

**Propagation:**

\[ RM^* + M \xrightarrow{k_p} RM_2^* \]

\[ RM_n^* + M \xrightarrow{k_p} RM_{n+1}^* \quad R_p = k_p[M][M^*] \] (2)

**Termination:**

i. Combination

\[ RM_n^* + RM_m^* \xrightarrow{k_{tc}} P_{n+m} \quad R_t = 2k_{tc}[M^*]^2 \] (3)

ii. Disproportionation

\[ RM_n^* + RM_m^* \xrightarrow{k_{td}} P_{n+p_m} \quad R_t = 2k_{td}[M^*]^2 \] (4)

or generally:
In the above expressions, \([I]\) and \([M]\) are the initiator and the monomer concentrations respectively and \(k_i\), \(k_p\), \(k_{tc}\), \(k_{td}\) and \(k_t\) are rate constants for initiation, propagation, termination through combination, termination through disproportionation and overall termination respectively. The factor \(f\) is the initiator efficiency, which takes into account the fact that not all of the radicals produced initiate a chain. If a stationary state with respect to the free radical concentration could be assumed, the rate of radical production must equal the rate of radical termination. Under these conditions the rate of polymerization can be obtained as

\[
R_p = -\frac{d[M]}{dt} = k_p f \frac{k_d}{k_t} [I][M] \tag{6}
\]

The heat of polymerization of acrylamide is \(-19.8\) Kcal/mole [75] and the temperature dependence of the heat and the free energy of reaction have been reported as [88]:

\[
\Delta H_T = 4321.296 - 27.764T + 0.44T^2 \text{ Kcal/mole}
\]

\[
\Delta G_T = 4321.296 - 27.764T \ln T - 0.44T^2 - 159.729 T \text{ Kcal/mole}
\]

The activation energy for persulfate initiated polymerization was reported to be \(15.2\) Kcal/mole [89].

Recently, in order to achieve a better control of the molecular weight and also to facilitate purification of the polymer, reactions in precipitating media for the polymer have been actively investigated. Dimethylsulfoxide - \(H_2O\)
[90], t-butanol [91], inverse suspension [92], tetrahydrofuran and water [93], and hexane [94] have been used among others. Typically, lower reaction rates and molecular weights are obtained. At the same time the chances of producing crosslinked polymer are also minimized.

Typical methods of determination of acrylamide in a monomer-polymer mixture are: NMR and ESR methods [95], iodometry [96,97], spectrophotometry [98], differential pulse polarography [99] and high performance liquid chromatography [100]. The molecular weight-intrinsic viscosity relationships for polyacrylamide have been reported to be [101]

\[
\eta = 4.9 \times 10^{-4} M^{0.8} \text{ at } 25^\circ C \text{ in water} \quad (7)
\]

\[
\eta = 7.19 \times 10^{-4} M^{0.77} \text{ at } 25^\circ C \text{ in 0.5M aq. NaCl solution.} \quad (8)
\]

\[
\eta = 1.36 \times 10^{-2} M^{0.54} \text{ at } 25^\circ C \text{ in ethylene glycol where } \eta \text{ is in (dl/g).} \quad (9)
\]

Hydrolysis of polyacrylamide in acidic medium causes almost quantitative conversion to polyacrylic acid.

\[
\begin{align*}
\text{H} & \quad \text{CH}_2-\text{CH} \rightarrow_n + n \text{H}_2\text{O} \quad \frac{\text{H}^+}{\text{C}=\text{O}} \\
\text{NH}_2 & \quad \text{CH}_2-\text{CH} \rightarrow_n + n \text{NH}_3
\end{align*}
\]
In basic medium the extent of hydrolysis is dependent upon the severity of the conditions. Partially hydrolyzed polyacrylamide is then obtained:

\[
\begin{align*}
\text{CH}_2-\text{CH} \quad \rightarrow \quad \text{CH}_2-\text{CH} - m \text{NaOH} \quad \rightarrow \quad \text{CH}_2-\text{CH} + q \text{NH}_3
\end{align*}
\]

Alternatively, acrylamide can be polymerized in alkaline medium [102-104] or in a mixture with sodium acrylate [105] to yield partially hydrolyzed polyacrylamide. Aqueous solutions of the above two polymers are much higher in viscosity than those of ordinary polyacrylamide at the same concentration, but are also very susceptible to the ionic strength of the solution.

Since the presence of oxygen is detrimental to the polymer chain length, a recent patent [106] suggests a method of inactivating dissolved molecular oxygen.

As mentioned previously, polyacrylamide can be cross-linked in the presence of suitable additives e.g., aldehydes [107], methylene bis-acrylamide or diethylene glycol diethyl ether [108], agarose [109], spontaneously at temperatures above 140°C [110], etc. The general mechanism for crosslinking can be shown as:
Such links would extend in 3-D. Electrolysis of acrylamide in H₂O in the presence of NaNO₃ leading to gel formation has also been reported [111]. The gelation of partially hydrolyzed polyacrylamide occurs through chelation of carboxylic groups in the presence of a polyvalent cation,

Thermally reversible gels have also been reported [112].
The process of crosslinking has been described in terms of crosslink density — number of crosslinks per original macromolecule [113] — mean field theory [114,115] in statistical mechanical terms and kinetic theory [116,117], but unfortunately there are only two reasonably satisfactory methods of characterization of a gel. Since a crosslinked polymer — which is essentially a single macromolecule — is insoluble in solvents and has no end group, the only properties amenable to investigation are its stress-strain response [118] and the crosslink density (calculated from the remaining amount of the crosslinking agent initially added).

An interesting insight into the process of crosslinking is afforded by a recently propounded theory of intramolecular crosslinking [119-122]. According to this theory, long chain polymer molecules, in the initial stages of crosslinking, would preferentially establish crosslinks among their own segments for the reasons of proximity. Such intramolecular bonds would reduce the effective length of the polymer chain. As a result, the viscosity of a polymer solution is expected to drop before gelation.

It is quite logical to assume that polymer molecules will not crosslink unless they are in sufficient concentration to ensure their entanglement with each other. Such a behavior is indicated by an abrupt increase in the slope of log (viscosity) - vs. - log (concentration) line for solutions of a polymer of given molecular weight [123]. The
concentration corresponding to the break point is termed critical concentration $C^c$. Since larger molecules will start entangling at smaller concentrations $C$ etc., it was proposed that the expression applicable at the break point would be [121]:

$$N C^a_c = N_c C^a = \text{constant}$$  \hspace{1cm} (10)

where $N$ is the number of monomer units in an average polymer chain (DP), and $a$ is a constant, characteristic of the polymer-solvent system. Theoretical attempts [124] have been made to discern the nature of and evaluate $a$ and the constant.

A3. Radiation Polymerization and Crosslinking of Acrylamide

The essential effect of radiation is to produce free radicals (and stable ionic species in rare instances) in the medium at much lower temperatures than those necessary for peroxide and redox initiators. The reaction mechanism is, therefore, the same as in conventional free radical reactions (equations 1-6), and also:

$$R_p = -\frac{d[M]}{dt} = k_p (f \frac{k_d}{k_t})^b[M]$$  \hspace{1cm} (6)

In dilute solutions, since the solvent molecules will be predominant in number, the so-called 'indirect effect' is operative. It means that the radiation energy is primarily absorbed by the solvent molecules and the free radicals consequently generated will attack the solute molecules.
Thus the term $R_i = 2f k_d[I]$ assumes a different meaning in this context. $[I]$ now becomes the radiation dose rate, expressed in eV absorbed per gm. of solution per unit time, and $2f k_d$ signifies the number of chains initiated per 100 ev/gm of solution absorbed. This last term is also called the G value for the polymer chains, if specified in terms of entities formed or destroyed per 100 eV absorbed by the solution. Equation (6) can now be rewritten as

$$R_p = \frac{k_p}{k_t} (G_i[I])^{1/2}[M] \tag{11}$$

One interesting aspect of radiation induced reactions concerns the overall activation energy. For a bimolecular termination reaction:

$$E = \frac{E_i}{2} + E_p - \frac{E_t}{2} \tag{12}$$

where the subscripts $i$, $p$ and $t$ mean initiation, propagation and termination respectively. Since, in the case of radiation initiation $E_i = 0$; (ordinarily $E_i$ is -30 Kcal/mole), it can be seen that the overall activation energy is far lower in this case than in the case of, for example, peroxide initiated reactions. The implication is that radiation induced reactions can be conducted at a much higher rate [125] without any danger of thermal runaway.

In the radiolysis of water $H_2O_2$, $H_2$, $H$, $e^{-}_{aq}$, OH and $HO_2$ are produced [126]. These species would then react with
the monomer and polymer in the aqueous solution in the manner specified earlier. It could be argued that the presence of H₂O₂ may be detrimental to the polymer molecular weight. Studies [127,128] on the equilibrium concentration of H₂O₂ in aqueous solutions of acrylamide have shown that at concentrations up to 10⁻² M acrylamide reacted with H and OH radicals (which would have reacted with H₂O₂) with increasing efficiency. This causes an increase in the equilibrium concentration of H₂O₂. At higher concentrations acrylamide starts trapping the precursors of H₂O₂, as a result G_H₂O₂ (number of H₂O₂ molecules produced per 100 eV absorbed) rapidly decreases and approaches zero.

The effect of radiation on monomers and polymeric systems was investigated with much interest after World War II [129-132]. A recent review [133] discusses various mechanisms of radiation induced reactions. Homogeneous polymerization of acrylamide in water by ionizing radiation [128, 134-136] and by photosensitization [137,138] were studied. Inhibition periods, observed in all experiments, were not very reproducible. The agreement between the results of Schulz [128] and Collinson et al., [134-136] was not satisfactory. Schulz reported the rate of reaction to be proportional to [M]¹.33 and [I]⁰.62 while Collinson et al., reported the dependency to be [M] and [I]⁰.5 (c.f. eqn. 6). The discrepancy could be due to inefficient deoxygenation,
or different methods of calculation of the reaction rate constant. In addition,

"These observations could indicate that a more complicated reaction mechanism actually takes place in the system which possibly involves a diffusion-controlled termination reaction. Indeed, water being a poor solvent for acrylamide, mutual interaction of two growing chains could be hindered by the coiling of growing polymer chains, without any visible phase separation ..." (p. 325, Ref. 131)

As reported later in this work, incipient phase separation was indeed observed, and the diffusion controlled nature of the reaction was also demonstrated.

It was also found [139] that at concentrations below 1M, the rate increased with monomer concentration, whereas in very concentrated solutions i.e., $>2.2M$ the reaction rate dropped as the concentration of the monomer was further increased. The reaction showed an acceleration period and a very marked 'after-effect'. This last phenomenon is described as the ability of the reaction to carry on even after the source of radiation has been removed. It is attributed to the slow reaction of the free radicals trapped in a viscous medium.

A study on the effect of dose rate on the molecular weight of polyacrylamide formed [140] indicated a dependence of $[I]^{-0.78}$ instead of the theoretically predicted $[I]^{-0.5}$. In another study [136] the intrinsic viscosity vs. molecular weight relationship for radiolytically formed polyacrylamide was found to be:

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These same authors also reported a [I]^{-0.21} dependence of the molecular weight on the dose rates. The difference between these results is remarkable.

Other patents and publications include radiation induced polymerization of acrylamide in the presence of NH$_3$ or ammonium salts [141-143], in acetone-water mixture [144-145], acrylamideurea adduct [146], in t-butanol-water [147], benzamide/banzenilide/phenanthrene [148], with acrylic acid and Na$_2$SO$_4$ [149], with sodium acrylate/acrylonitrile/sodium ethylene sulfite [150,151]. A patent [152] reported higher rates of reaction and higher molecular weights attained in the presence of NaCl or Na$_2$SO$_4$. Another patent [153] suggests polymerizing a monomer by dissolving a radioactive inert gas ($^{85}$Kr) under pressure and removing it from the product. Yet another [154] suggests initiating polymerization by radiation and completing it using a free radical catalyst. Two other patents claim preparation of solvent resistant surface coating using acrylamide, melamine, formaldehyde and Et$_3$N [155] and polymer foam from aqueous acrylamide [156]. Quantitative hydrolysis of radiation polymerized polyacrylonitrile to polyacrylamide at 5130-34,200 atm. pressure under $\gamma$ radiation has been reported [157].

\[
\eta = 6.8 \times 10^{-4} M_n^{0.66} \quad (13)
\]

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Effects of bulk mixing on the molecular weight distribution of radiation polymerized acrylamide has also been studied [158,159].

Under prolonged irradiation polyacrylamide formed in the acrylamide solution will start crosslinking. This is supposed to occur through imidization (p. 328, Ref. 131):

\[
\begin{align*}
\text{\( \left( \text{CH}_2\text{CH} \cdots \right)_n \)} & \quad \text{CH}_2\text{CH} \cdots \\
\text{C=O} & \quad \text{C=O} \\
\text{NH}_2 & \quad \text{NH}_2 \\
+ & \quad \text{NH}_2 \\
\text{C=O} & \quad \text{C=O} \\
\text{\( \left( \text{CH}_2\text{CH} \cdots \right)_m \)}
\end{align*}
\]

Alternatively, radical abstraction may occur under ionizing radiation, which could lead to intermolecular bonding:

\[
\begin{align*}
\text{\( \left( \text{CH}_2\text{CH} \cdots \right)_n \)} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{C=O} & \quad \text{C=O} \\
\text{NH}_2 & \quad \text{NH}_2 \\
\text{\( \left( \text{C-C} \cdots \right)_n \)} & \quad \text{C=O} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{C=O} & \quad \text{C=O} \\
\text{NH}_2 & \quad \text{NH}_2 \\
\text{\( \left( \text{C-C} \cdots \right)_m \)} & \quad \text{\( \left( \text{C-C} \cdots \right)_n \)}
\end{align*}
\]

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The latter process occurs without any evolution of ammonia.

It is worthwhile to make an interesting note here, that when the structure of a vinyl polymer is such that each carbon atom of the main chain carries at least one hydrogen atom (structure I); the polymer crosslinks, whereas if a tetrasubstituted carbon atom is present in the monomer unit (structure II), the polymer degrades upon irradiation (p. 355, Ref. 131).

Crosslinking of acrylamide solution in the presence of methylene-bis-acrylamide, triacrylamidylamine and ammonium persulfate has been reported [160]. Solutions of polyacrylamide have been gelled under continued irradiation [161, 162].

A4. Energy Transfer Characteristics of β Rays

Several expressions [163-166] have been proposed for the distribution of intensity of radiation around a point source of β particles. The most popular among these is the one by Loevinger [165] and its modified form is given by [166]:

\[
\begin{align*}
\text{H} & \quad \text{R}_1 \\
\text{CH}_2\text{C}_n \quad \text{CH}_2\text{C}_n \\
\text{R} & \quad \text{R}_2 \\
\text{(I)} & \quad \text{(II)}
\end{align*}
\]
\[ D(R) = \frac{K}{(\nu R)^2} \left\{ C[1 - \frac{\nu R}{C} e^{-\frac{R}{C}}] + \nu R_m 1 - \frac{\nu R}{C} - \nu R_m e^{-\frac{R_m}{C}} \right\} \quad (14) \]

where \( [1 - \frac{\nu R}{C} e^{-\frac{R}{C}}] = 0 \) for \( \frac{\nu R}{C} \geq 1 \)

\[ D(R) = 0 \quad R \geq R_m \]

and

\[ R = \text{distance from the source in gm./cm.}^2 \]
\[ \nu = \text{apparent absorption coefficient cm.}^2/\text{gm.} \]
\[ C = \begin{cases} 2.0 & 0.17 < E_0 < 0.5 \\ 1.5 & 0.5 < E_0 < 1.5 \\ 1.0 & 1.5 < E_0 < 3.0 \end{cases} \]

\[ E_0 = \text{maximum energy of } \beta \text{ particles in MeV} \]
\[ R_m = \text{maximum depth of penetration of } e^- (\text{gm./cm.}^2) \]
\[ D(R) = \text{energy absorbed in rads (100 ergs/gm.) at a distance } R, \text{ per disintegration.} \]

(It is a common practice in radiology to specify distances in gm./cm.\(^2\), to make them independent of the density of the medium. The true distance in cm. in any medium can be obtained by dividing the distance in [gm./cm.\(^2\)] by the density [gm./cm.\(^3\)] of the medium).

The normalization constant \( K \) can be evaluated from the requirement that the total energy absorbed by the medium within a distance \( R_m \) must be the average \( \beta \) particle energy per disintegration.
For $^{32}P$ the maximum and the average $\beta$ particle energy are 1.71 MeV and 0.70 MeV respectively. Therefore $C=1$, and $K$ can be calculated to be:

$$K=1.6987\bar{E}\nu^3/(3-(1-\nu R_m)e^{-\nu R_m^2}e^{-\nu R_m}) \text{ rads/hr-mCi}$$

(15)

The fact that 1 millicurie = $3.7 \times 10^7$ disintegrations per sec. has been taken into account and $\bar{E}$ is the average $\beta$ particle energy.

The maximum depth of penetration can be calculated from the following [167].

$$R_m (\text{gm./cm.}^2) = 0.412 E_0^n$$

$$n = 1.265 - 0.094 \ln E_0$$

(16)

The mode of disintegration of $^{32}P$ is:

$$^{32}P \longrightarrow ^{32}S \text{ (stable)} + \beta + \bar{\nu}$$

with energy of disintegration 1.71 MeV randomly divided between the $\beta$ particle and antineutrino. Half life of the process is 14.22 days [168]. The $\beta$ energy spectrum can be calculated from the conventional Fermi plots [169,170].

The value of $\nu$ to be used in equations (14) and (15) is given by [166]:

$$\nu = \frac{18.6}{(E_0-0.036)1.37} (2 - \frac{\bar{E}}{E^*}) \text{ cm.}^2/\text{gm.}$$

(17)
for tissue (density = 1 gm./cm.$^3$). $\bar{E}^*$ is the average $\beta$ ray energy per disintegration for a hypothetical allowed spectrum with the same value of $E_0$, for $^{32}\text{P}$, $\bar{E}/\bar{E}^* = 1.0$ and

$$C = 1$$

$$R_m = 0.7902 \text{ gm./cm.}^2$$

$$\nu = 0.1826 \text{ cm.}^2/\text{gm.}$$

$$K = 31759 \text{ rads/hr.-millicurie}$$

Given equation (14), the dose rate distribution inside or outside of a source of any shape can be ascertained by considering the source as a collection of point-sources. The model that is of interest to us is a long capillary filled with radioactive liquid, representing a pore in the reservoir rock. It is clear that, once the source dimensions are comparable to the maximum depth of penetration $R_m$ of $\beta$ particles, the source cannot be reduced to a point or line located at the center or axis of symmetry. A survey of the available literature shows that rigorous calculations have been done only in the cases of plane slabs, spheres and disks, each assumed to be uniformly loaded with the radioactive material [166]. More diverse source configurations have been considered in the case of $\gamma$ ray emitters e.g., ellipsoids [171] and a heterogeneous phantom [172]. Monte-Carlo techniques were applied in these calculations and the results were presented in tabular form. To the knowledge of the present author, no
analytical, graphical or tabular data exists in the reported literature, on the dose rate distribution inside a cylinder containing radioactive fluid.

B. Elucidation of the Problem

The idea for the present work came about during a discussion on tertiary oil recovery. As has been mentioned already, during oil recovery operations, certain undesirable geological formations are routinely plugged with crosslinkable chemicals. It was also mentioned that such indiscriminate plugging would lose the otherwise recoverable oil contained in the finer pores. A need was therefore felt to devise a method by which only those pores that are bigger than a certain diameter would be plugged while the finer ones would be left open to be swept by the pusher fluid. In other words, the desired process should ensure a higher rate of crosslinking (or rate of reaction) in the larger pores than in the smaller ones. A solution to this problem was found in the fact that $\beta$ (and also $\alpha$) radiation has a finite depth of penetration in a given medium.

Imagine a uniform concentration of radioactive particles dissolved in water containing a polymerizable (or better still crosslinkable) monomer. Consider now a small volume element in this medium (Figures 1-A and B). Only those electrons that are emitted by radioactive nuclei lying within a sphere of radius $R_m$ (maximum depth of penetration
Figure 1. Distribution of sources for a fluid element in (1A) an infinite reservoir and (1B) a finite reservoir.
of the \( \beta \) rays) will be able to reach this fluid element and transfer a part of their energy to it (equation 14). Any radioactive source located beyond this critical distance will have no effect on this volume element. Now, if this element were situated in a radioactive medium contained inside an infinitely long cylinder such that the diameter of the cylinder is less than the critical distance \( R_m \) (Figure 1-B) then, since there are no radioactive sources in the hypothetical sphere beyond the wall of the cylinder, the fluid element in effect has lost the energy that could have come from the radioactive sources contained in the part of the sphere outside the cylinder. In other words, the same volume element in a medium of identical radioactivity will receive different energies depending upon the size and shape of the container. This difference in absorbed energy should be manifested by different rates of reaction of the monomer dissolved in the fluid.

In order to calculate the number of nuclei contributing energy to a fluid element located anywhere inside the cylinder (of radius \( a \)) containing the radioactive fluid; we need to know the fraction of surface area of a sphere of radius \( R \) \( (0 \leq R < R_m) \), which is contained inside the cylinder, if the sphere were centered at the fluid element. Appendix D shows the steps involved in this calculation.
C. Purpose of the Work

The purpose of this work is twofold:

1. To demonstrate experimentally and from theoretical considerations that different rates of reaction would exist in reactive radioactive fluids contained in capillaries of different diameters.

2. To examine the effect of salt and high temperature on the reaction characteristics of aqueous solutions of acrylamide subjected to irradiation.
II. EXPERIMENTAL

A. Set-Up for External Irradiation

The external irradiation experiments were carried out in a $^{60}\text{Co}$ irradiation facility located in the Nuclear Science Center. A 600 curie source, which has $^{60}\text{Co}$ pellets packed inside the annulus of a cylinder was used.

Mechanical arrangements facilitated motorized lowering and raising of a water-tight cylindrical vessel into the hollow of the annulus, the dimensions of the former being such as to ensure a snug fit into the latter. The samples to be irradiated could be kept inside the vessel. For irradiation at high temperatures, the samples were kept in a temperature bath which was in turn placed inside the above mentioned vessel. The temperature bath was a cylindrical canister with 1/32" thick stainless steel wall and a lid. This canister was partially filled with water which could be heated to provide and maintain the desired temperature in the vapor space where the samples were kept. Heating was accomplished through a heating tape wrapped around the bottom portion of the canister and the current through the tape was controlled by a rheostat (Figure 2).
Figure 2. $^{60}$Co irradiation set-up.
Thus, only the walls of the vessel and the canister came between the source and the samples. The temperature in the vapor space was monitored by a copper-constantan thermocouple placed close to the samples. The temperature could be controlled to \( +1.5^\circ C \) in this set-up.

**B. Set-Up for Internal Irradiation**

In order to examine the effect of diameter on the viscosity of the solution, the internal irradiation experiments were carried out in capillary tubes containing the required amounts of dissolved \(^{32}\text{P}\), acrylamide and salt. The internal diameters of the capillary tubes used were 0.038 (teflon), 0.086 (teflon), 0.229 (tygon) and 0.60 (glass) cm. Since the minimum amount needed for a viscosity reading was approximately 1.2 ml., the required length of these tubes were calculated to be 1058, 207, 29 and 4.3 cm. respectively. The long tubes were wrapped on a 15 x 15 cm. square wire screen such that the parallel segments of the tubes were \(- 0.6 \text{ cm.} \) apart. These wire screens were stacked on top of each other such that they were at least 3.5 cm. apart and this rack was then submerged in a thermostatically controlled temperature bath containing 90:10 water:glycerine mixture. The temperature in this bath was maintained at \( 80 \pm 0.5^\circ C \) with occasional replenishment of water which was lost by evaporation. The presence of glycerine in the bath kept this loss to a minimum.
In order to minimize end effects in the case of 0.6 cm. diameter capillary, a total sample volume of 6 ml. was used for it. This gave a length to diameter ratio of 7.0. The glass capillary was formed into a U shape, the ends of which were joined together with a rubber tube to keep evaporation losses to a minimum.

C. Materials

Polyacrylamide (MW 5-6x10^6) was obtained from Poly-science and was used as received.

Fricke solution for dosimetry studies was prepared in accordance with that suggested by Allen [1]. 0.8 g. Fe (NH₄)₂(SO₄)₂·6H₂O and 0.12 g of NaCl and 44.0 ml. of 98% H₂SO₄ were added to sufficient distilled water to make two litres of solution. Oxygen was bubbled through the solution for approximately five hours to ensure saturation. The solution was stored in a colored bottle and used while it was still fresh.

A 50 millicuries batch of radioactive ³²P (purity 99.9%) was obtained from New England Nuclear in the form of orthophosphoric acid in 1 ml. of 0.02 N hydrochloric acid. It was neutralized by 0.1 N NaOH using neutral red as an indicator.
D. Procedure

D1. Sample Preparation and Exposure

All concentrations are expressed in weight/volume. Distilled water used in the experiments was first boiled for about 15 minutes to deoxygenate it and required amounts of salt and monomer added while it was still warm. It was mixed well, filtered immediately and stored in bottles under nitrogen in the dark. Prior to irradiation approximately 20 ml. portions of the solution were transferred to scintillation vials under nitrogen. The vials were then exposed to radiation at labeled positions. At the end of the desired period of exposure they were opened and their viscosities and extents of conversion of monomer measured. Except for 1.5% monomer (0, 5 and 10% salt) solutions, all samples were subjected to uninterrupted exposure for the duration. In the case of 1.5% acrylamide solutions, the samples were pulled out from the irradiation chamber, opened, a sample taken in a syringe for viscosity measurements, closed and returned to the irradiation chamber within ten minutes.

For irradiation at high temperature the vessel with samples inside the canister was submerged in water, and checked from time to time to ensure that the inside temperature was a steady ~80°C, after which it was lowered into the irradiation chamber. A temperature variation of ±1.5°C was noticed during the irradiation period.
Only 3% acrylamide in 10% salt solution was used in the case of internal irradiation experiments. The neutralized radioactive solution was diluted to the mark in a 10 ml. volumetric flask by the addition of 10% salt solution. Its initial specific activity was therefore 5 millicurie/ml. which diminished according to the law of radioactive decay with a half life of 14.22 days. Appropriate quantities of this solution (depending upon the time the mixture was prepared) and 6% acrylamide in 10% salt and 10% salt solutions were mixed in a beaker to obtain a solution containing 3% acrylamide, 10% salt and 1 mCi/ml. of radiation. Approximately 1.2 ml. portions of this solution were then sucked into different capillaries and the ends of the capillaries were shut by melting them on a burner. The seals were then tested for pressure by squeezing them very carefully, after which they were wrapped on the previously described wire screens.

D2. Dosimetry for External Irradiation

Dosimetry studies were done in identical geometry to the samples. Three different arrangements were used depending upon the temperature and convenience. These were (a) sample at the center, (b) samples at three corners of a square and (c) samples situated at the corners of a regular octagon. It was found that the intensity of radiation varied not only in the vertical direction due to the finite height of the $^{60}$Co packed annulus (as
reported by Barnes [175], but it also varied in the horizontal plane because of the presence of other sources in the pool (Figure 4). In order to determine the dose rate at any given point, Fricke solutions in scintillation vials were exposed for specified time intervals up to 60 minutes. The quantity of ferric ions produced during these intervals was determined by measuring the optical absorbance of the solutions at 305 μm with an ultraviolet spectrophotometer. From the known molar extinction coefficients and its temperature dependence, the concentration of Fe\(^{3+}\) ions was calculated as (c.f. Spinks and Woods [16]).

\[
C = - \frac{\log \tau}{2201 \left[1+0.007(T-25)\right]} \text{ mole/liter}
\]

where \(T\) is the temperature in °C at which the absorbance readings are taken and \(\tau\) is the fractional transmittance. From a plot of \(C\)-vs-\(t\) and the fact that 15.5 ferric ions are formed for every 100 ev absorbed, the dose rate \(D\) can be found to be:

\[
D = 6.079 \times 10^7 \left(\frac{dC}{dt}\right) \text{ rads/min}
\]

where \(t\) is in minutes.

In order to avoid cluttering of the graph one of the calibration curves prepared in this manner is shown in Figure 3. The dose rates at various points on a horizontal plane inside the vessel are also shown in Figure 4.
Figure 3. Typical Fricke-Dosimetry response to the $^{60}$Co irradiation.
Figure 4. Dose rates at various points inside the irradiation chamber.
D3. Dosimetry for Internal Irradiation

The total dose absorbed by the capillaries containing the radioactive fluid can be calculated from [c.f. 168]

\[ D = 35.56 \frac{\bar{E}}{\rho} \frac{C_0}{\phi_a} (1-e^{-\lambda t}) \text{ rads} \]  \hspace{1cm} (19)

where

\[ \bar{E} = \text{average energy of the } \beta \text{ particles } 0.695 \text{ MeV} \]
\[ \lambda = \text{radioactive decay constant} = \frac{0.693}{t_{1/2}} \]
\[ t_{1/2} = \text{half life} = 2.048 \times 10^4 \text{ min.} \]
\[ t = \text{time elapsed in min.} \]
\[ C_0 = \text{initial activity in millicuries/ml.} = 1.0 \]
\[ \rho = \text{density of the solution} = 1.13 \text{ gm./ml.} \]
\[ \phi_a = \text{correction factor to account for the fraction of total emitted energy absorbed by a tube of radius } a \]

or upon substitution of these values:

\[ D = 6.463 \times 10^5 (1-e^{-3.385 \times 10^{-5} t}) \phi_a \text{ rads} \]  \hspace{1cm} (20)

At the end of predetermined periods, the tubes were unwrapped from the wire screen, both ends snipped and the solution pushed out with the help of a syringe into the viscometer.

D4. Viscosity Measurement

Viscosities of all samples (except for those polymerized in 0.6cm. dia. tube) were measured at 25°C in a Brookfield cone
and plate viscometer. The following relationships were used to convert the dial reading to viscosity in centipoise.

\[
\text{shear stress} = \frac{3T}{2\pi r^3}
\]

\[
\text{shear rate} = \frac{2\pi w}{60 \sin \phi}
\]

\[
\text{viscosity} = \frac{\text{shear stress}}{\text{shear rate}}
\]

where

- \(T\) = torque applied = \(k\theta\)
- \(\theta\) = dial reading
- \(r\) = radius of the cone = 2.40 cm
- \(w\) = rpm of the cone
- \(\phi\) = angle of the cone = 1.57°
- \(k\) = spring constant = 673.7

Substituting for these variables, we obtain

\[
\mu = 6.09 \frac{\theta}{w} \text{ centipoise}
\]

The internally irradiated sample in 0.6 cm. glass tube was used repeatedly for viscosity measurements. A rolling ball viscometer was used for this purpose. It consisted of a 15 cm. long glass tube of internal diameter 0.7 cm. and it was inclined at an angle of 30° from the horizontal. The time taken by a \(\frac{1}{4}\)" chrome-steel ball to roll down the middle 10 cm of the tube was taken as an
index of the viscosity of the solution. This viscometer was later standardized by comparing the roll time versus the viscosity obtained on the Brookfield viscometer.

Viscosity measurements of the solutions in other capillaries were made directly on the Brookfield viscometer.

D5. Determination of the Extent of Reaction

An iodometric method of determination of the number of double bonds in acrylamide [96,97] was used to follow the course of reaction. After irradiation, 6 ml. of 1% or 3 ml. of 2% or 2 ml. of 3% acrylamide solution was transferred to a 125 ml. erlenmeyer flask equipped with a ground glass joint. To this was added 10 ml. of 0.25N bromate-bromide solution (containing 6.96 g. of KBrO₃ and 2.5 g. of KBr per litre) and the flask was cooled to sub-zero temperature. Approximately 3 ml. of 0.2N H₂SO₄ was added to this cooled mixture, the flask was quickly stoppered and kept in the dark for at least 30 minutes with frequent shaking. To avoid losses of Br₂, the flask was cooled again before opening and approximately 3 ml. of 20% KI solution was added to the flask. The contents of the flask were then titrated to a colorless end point with 0.1N Na₂S₂O₃. No starch was added because it was found that in the presence of a significant amount of polymer, addition of starch caused multiple end points.
From the reactions occurring in the system,

\[
\begin{align*}
5 \text{KBr} + \text{KBrO}_3 + 3\text{H}_2\text{SO}_4 & \longrightarrow 3 \text{K}_2\text{SO}_4 + 3 \text{H}_2\text{O} + 3 \text{Br}_2 \\
\text{Br}_2 + (1-x) \quad \text{CH}_2=\text{CH}-\text{C}-\text{NH}_2 & \longrightarrow (1-x) \quad \text{H}_2\text{C}-\text{CH}-\text{C}-\text{NH}_2 + x \text{Br}_2 \\
x \text{Br}_2 + y \text{KI} & \longrightarrow 2x \text{KBr} + (y-2x) \text{KI} + x \text{I}_2 \\
x \text{I}_2 + 2x \text{Na}_2\text{S}_2\text{O}_3 & \longrightarrow 2x \text{NaI} + x \text{Na}_2\text{S}_4\text{O}_6
\end{align*}
\]

the extent of reaction \(x\) (fraction of initial acrylamide consumed) may be calculated as follows

\[
x = 0.592 N_1 V_1 - 0.480 \tag{22}
\]

where \(N_1\) is the normality of the \(\text{Na}_2\text{S}_2\text{O}_3\) solution as determined in a blank run against the bromate solution and \(V_1\) is the volume in ml. of \(\text{Na}_2\text{S}_2\text{O}_3\) solution needed to react with the freed \(I_2\).

A few words concerning the accuracy of the experimental results should be mentioned here. It is commonly accepted \([174]\) that the accuracy of dosimetry experiments is \(+5.0\%\). First few experiments on the relative viscosity vs. dose were done in triplicates and the results obtained were within this experimental error. Subsequent experiments were then carried out following the exact procedure.

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III. DISCUSSION OF RESULTS

Since conditions inside the oil reservoirs are characterized by high temperature and salinity (Schumacher, [38]), the solutions in the experiments with various size capillaries were kept at 80°C and contained 10% salt. Only viscosity measurements were made for these solutions which contained dissolved $^{32}$P. Safety considerations precluded the pragmatics of determining the extent of reaction in these experiments. However, these were measured from experiments conducted under similar conditions but irradiated externally with $^{60}$Co. The implication was that the course of the reaction is the same whether it is induced by external irradiation or by dissolved radioactive particles in the solution. To evaluate the influence of temperature and the presence of salt, experiments were run also at room temperature and with varying amounts (0, 5 and 10%) of salt in the solution. The results are presented in tabular form in Appendix A and in graphical forms at appropriate locations in the text. Since the monomer solutions at 81°C did not crosslink, attempts were also made to bring about crosslinking of these


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solutions in the presence of various additives, and these observations are summarily reported in Appendix B.

A. Irradiation of Acrylamide Solutions at Room Temperature with $^{60}$Co

Al. Effect of Monomer Concentration on the Viscosity of Solution

The variations in the relative viscosities of the solutions containing the polymerizing monomer, as a function of dose received are shown in Figure 5. Four different concentrations of the monomer (1, 1.5, 2 and 3% w/v) containing no salt were used for these experiments. The numbers along the curves represent % conversion of monomer. Only 1.5% acrylamide samples were interrupted in their exposure to radiation. Relative viscosities of samples initially containing 3%, 2% and 1.5% acrylamide (shown more clearly in Figure 6), all increased to eventually form a cross-linked polymer (as indicated by their insolubility in water, and the fact that air bubbles could not rise in them). A 1% acrylamide solution did not crosslink (Figure 7). From the procrastination exhibited by the viscosity of 1.5% acrylamide solution to rise, it appears that the minimum concentration of monomer needed to form a cross-linked polymer is approximately 1.5% w/v. Since $\text{DP}_a[M]^a$ where $a \approx 1.0$, it is quite possible that the polymer molecules formed at monomer concentrations less than 1.5%
Tables A-1, 2, 3, 4

- △ 1% ACRYLAMIDE
- ○ 1.5%
- ● 2%
- ○ 3%

Figure 5. Relative viscosities of acrylamide solutions of different concentration vs. dose from $^{60}$Co at 28°C. (Fractions denote fractional conversions at those points.)
Figure 6. Relative viscosity of 1.5% acrylamide solution in salt water vs. dose from $^{60}$Co at 28°C.
Figure 7. Relative viscosity of 1% acrylamide solution in salt water vs. dose from $^{60}$Co at $28^\circ$C.
are not long enough (and sufficient in number per unit volume) for any appreciable entanglement which is a prerequisite for crosslinking. Katayama et al., [175] concluded from their studies on the proton magnetic relaxation time of water in acrylamide gel that the minimum concentration of monomer needed for gel formation was 2.8%. They did not observe any such inversion in the relaxation time when the samples were thoroughly degassed, and made no attempts to investigate the dependence of this minimum concentration upon the dissolved oxygen content. In the light of the experiments conducted in the present study where crosslinked gels could be obtained at monomer concentrations as low as 1.5%, the discrepancy can be resolved in two ways. The first, that the minimum in the relaxation time is dependent upon the concentration of dissolved oxygen and/or the second, that the water protons in acrylamide gels containing less than 2.8% polymer are not "free". Further experimentation is needed to confirm either or both of the proposals.

A couple of intriguing features concerning the viscosity-vs.-dose relations of potentially crosslinking solutions stand out in Figure 5. The initial rate of increase of solution viscosities showed a marked dependence on monomer concentration. Again, since higher monomer concentrations not only lead to longer macromolecules but also aid in the rate of reaction, both of these factors

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worked to enhance the viscosity of the solution. The other interesting point to be noted is the viscosity plateau reached by all three solutions before gradual crosslinking caused an almost exponential leap in the viscosity. At first it was thought that the hold in viscosity was caused by some form of molecular rearrangement (possibly a second order crystalline transition) which might be a prerequisite to the formation of 3-D crosslinked gel. To test this hypothesis, samples were taken from 3% acrylamide solutions containing 0, 5, 10% sodium chloride and also 1.5% acrylamide solutions which had been polymerized just beyond the plateau. They were prepared for x-ray studies by slow evaporation of water at room temperature. Beautiful dendritic patterns characteristic of salt deposits were obtained in the case of samples containing salt. An x-ray crystallogram for all samples showed peaks corresponding to the 200 and 400 planes in salt crystals and a broad and weak hump in the base line which indicated that the polymer was essentially amorphous. Nevertheless, it was noted that quite large (~2 mm. side) undeformed single crystals of salt could be grown in a viscous medium and that salt exhibited a preferential tendency to orient in 200 and 400 planes.

The arrest in the viscosity increase can be rationalized with the help of the theory of macromolecular domains (Aharoni, [119-122]). As discussed earlier, the
random coil model of the polymer chains predicts a monotonic increase in the solution viscosity as crosslink density increases. But based on the collapsed coil model (Aharoni, [119-122]), intramolecular crosslinks could be formed in polymer solutions where the concentration of polymers is above the critical concentration (~1.5% as determined previously). Because of the reduction in effective chain length of a polymer subjected to such intramolecular bonding, the solution viscosity is expected to decrease. Such dramatic effects on route to gelation would be masked if the concentration of polymers was much more than the critical concentration because the entangled molecules could equally readily form bonds to their nearest neighbors. The phenomenon is therefore expected to be observed more clearly in the vicinity of the critical concentration. This could be the reason why the characteristic dip is present in the case of 1.5% and 2% monomer solutions and that it is not so prominent in the case of 3% monomer. The relative frequency of intermolecular and intramolecular crosslinking can also account for the decreasing span of the viscosity plateau with increasing concentration of monomer in solution. The dip in the viscosity curve can be magnified by gelation of a solution containing low concentration ($c_{\text{critical}}$) of a high molecular weight polymer. This is indeed observed to be the case with polyacrylamide as mentioned later in this work.
It should be mentioned at this point that the polymers in the monomer solution exposed to radiation showed some tendency to settle as they formed. This was true, irrespective of the monomer concentration, salt content or the temperature of reaction. It was noticed upon very careful examination that the solution would split into two almost indistinguishable phases, the lower phase being much more viscous than the upper one. It was difficult to quantify this phenomenon because even the slightest shaking (e.g., raising the samples from the $^{60}$Co pool, bringing the samples to the laboratory on foot) distorted the phase boundary and complete mixing occurred either upon shaking it a bit more or letting it stand for a day or so. In one case (3% monomer) the volumes of the bottom phases were 11.1 ml. (74%), 12.6 ml. (84%), 13.6 ml. (91%) for 15 ml. solutions containing 0, 5 and 10% salt. This sample was polymerized up to a point ($9.7 \times 10^4$ rads) just before the plateau. In another case (3% monomer, no salt, $\sim 9 \times 10^4$ rads) the volume fractions of the two phases were almost equal, the relative viscosity of the top layer was $\sim 2.0$, that of the bottom layer was $\sim 175$, while the relative viscosity of the mixed solution (which now contained roughly 1.2 ml. less of each phase) was $\sim 40$. All the results reported in this work were obtained after thorough mixing of the two phases.
Once beyond the plateau, the samples rapidly proceeded to form crosslinks, the rate of increase of viscosity again exhibited the anticipated dependence on monomer (or now polymer) concentration. As the samples crosslinked, several peculiar phenomena were observed. First, the formation of a substantial amount of crosslinking was accompanied by irregular viscosity readings, rising bubbles in the solution appeared to be avoiding invisible planes, and the solution would flow as one single blob if it were poured into another container. This behavior was labeled as an indication of the onset of gelation (as distinguished from gel effect which occurs much earlier than crosslink formation), its characteristic being that the polymer has just enough crosslinks to render it water insoluble. Figure 8 represents the total dose needed to effect such a condition for a given initial concentration of the monomer. This figure is approximate in nature since it is very difficult to determine the degree of crosslinking in a sample.

Soon after the onset of gelation the samples started shrinking in volume and expelling the water contained inside. The viscosity of the expelled water decreased as crosslinking continued; also, samples with lower initial monomer content dispelled fluid of higher viscosity than samples with higher initial monomer content. Both of the
Figure 8. Total dose needed to crosslink an aqueous solution of acrylamide at 28°C under 60Co.
above observations could result from the fact the gel boundary was less clearly defined in the case of low initial monomer content and thus the fluid surrounding it was more viscous. As shrinkage continued the gel boundary became more defined and only water was expelled. Following the same logic, it can be seen that samples with lower initial monomer content will expel more water than their more concentrated counterparts. This behavior is compared in Figure 9 for two samples (2.0% and 5% initial acrylamide concentrations). Similar results on crosslinking and shrinkage of gel upon irradiation have been reported (Alexander and Charlesby, [161]) starting with poly(acrylamide), poly(acrylic acid), poly(vinyl alcohol) and poly(vinyl pyrrolidone).

The gels with higher initial monomer contents were more transparent (glass like) and tougher than those formed from lower initial monomer content. At present, there is no explanation for the difference in clarity of the gels.

The expelled water was periodically removed and samples were exposed to further radiation and kept shrinking in volume. The physical appearance did not change much except that the samples got tougher. No evolution of NH₃ was noticed although bubbles did form in the matrix. When these bubbles were removed with the help of a fine syringe, the gel around them collapsed in extremely thin planes.
Figure 9. Fraction of total water expelled from the gel vs. dose absorbed after crosslinking at two different initial concentrations of acrylamide under 60Co.
The orientation of these planes, which could be only seen from an angle, were random. No popcorn formation — indicative of imidization — as reported by Chapiro (Ref. 131, p. 328) was observed. It can therefore be concluded that crosslinking occurred with little or no imidization. It is possible that higher initial monomer concentrations than used in this report are a prerequisite for imidization.

These gels were brittle in the beginning and, when broken, the two faces had the appearance of a composite plane containing numerous crystallites. As the irradiation continued it turned into an extremely hard and tough mass which was still clear as glass. One such block (~7.5 cm. dia x 6.0 cm. high) made from 20% acrylamide was allowed to stand in a pool of methanol for more than a month. A milk white and rigid plastic was obtained which did not break even if hammered. Upon sawing a slice of it, it was observed that methanol had diffused only about \( \frac{1}{4} \) cm. into the gel. The gel slowly turned transparent again when removed from methanol bath and exposed to air, but retained its resiliency. Nails and screws could be driven through it without cracking it.

A2. Effect of Salt on the Viscosity of the Solution

Figures 6, 7 and 10 show the effect of salt content on the relative viscosity of polymerizing solutions containing 1, 1.5 and 3% monomer. Again 1% solution showed
Figure 10. Relative viscosity of 3.0% acrylamide solution in salt water vs. dose from $^{60}\text{Co}$ at 28°C. (Fractions denote fractional conversion at those points.)
negligible change in viscosity as the salt content was increased. For both 1.5% and 3% solution increasing amounts of salt enhanced the initial rate of increase of relative viscosity. At the same time, the samples crosslinked much faster in the presence of salt than in its absence.

Using the expression

\[ V = 1.00138 + 16.6253 m + 1.7738 m^{3/2} + 0.1194 m^2 \]

where \( V \) is volume of solution in ml./1000 g. \( \text{H}_2\text{O} \) and \( m \) is the molality of salt in the solution; the volume occupied by salt molecules in 5 and 10% w/v salt solutions can be calculated to be 1.65 ml. and 3.5 ml. per 100 g. of water respectively. The net decrease in the volume available to the polymer molecules is of the order of 0.1–0.2% only. Thus, the increased viscosity of saline solutions of polymer cannot be said to be associated with an increase in effective concentration of the macromolecules.

The higher rate of increase of solution viscosities with higher salt contents seems to be a direct result of higher rates of reaction achieved in saline solutions. When the influence of faster reaction on the solution viscosity is taken into account in the form of a graph of \( \eta_{\text{rel}} \) vs. extent of reaction (Figure 11), it is seen that the response curves for all three salt concentrations merge into one. This means that in all three solutions, the same amount of polymer is needed to attain a given
Figure 11. Relative viscosity vs. fractional conversion of 3\% acrylamide solutions in salt water at 28°C and 81.5°C under $^{60}$Co irradiation.
and this is made up by different rates of reaction in media of different salinity. It can therefore be said that the presence of salt has no effect on the viscosity of the polymerizing solution. An additional conclusion can be drawn from the observation that higher extents of reaction were needed to reach the viscosity plateau in solutions of higher salinity. If, as discussed in the last section, the occurrence of the viscosity plateau were taken to be an indication of macromolecular entanglement, the above observation indicates that the hydrodynamic volumes of macromolecules in saline solutions are smaller than those in pure water. This realization makes it difficult to explain why the same amount of polymer with smaller hydrodynamic volumes would exhibit the same solution viscosity and would crosslink sooner than its more expanded counterpart. Thus, even though the presence of salt had no effect on the solution viscosity, the exact nature of its influence is difficult to determine.

A3. Effect of Monomer Concentration on the Rate of Reaction

As discussed earlier the expression for the rate of a radiation induced free radical initiated reaction is given by

\[ R_p = \frac{d[M]}{dt} = \frac{k_p}{k_t} \frac{1}{x} (G_1 I)^{\frac{1}{k}} [M] \]  

(11)

upon integrating from \( t=t_i \) to \( t=t \)

\[ -\ln \left( \frac{[M]}{[M_o]} \right) = \frac{k_p}{k_t} \frac{1}{x} (G_1 I)^{\frac{1}{k}} (t-t_i) \]
where $t_i$ is the induction period (or dead time) before the reaction actually starts. Since

$$x = 1 - \frac{[M]}{[M_0]}$$

we can write

$$- \ln(1-x) = \frac{k_0}{k_i} (G_i I_0)^{1/2} (t-t_i)$$  \hspace{1cm} (23)

$$= k^{1/2} (t-t_i)$$  \hspace{1cm} (24)

where $k$ is the overall rate constant. This expression predicts that a plot of $-\ln(1-x)$ vs $t$ should be a straight line with a dead time equal to $t_i$. Figures 12 and 13 are $x$ vs $t$ plots for monomer concentrations of 1, 2 and 3% and also 3% with 0.5 and 10% salt at 28°C. Figures 14 and 15 depict $-\ln(1-x)$ vs $t$ behavior of these same solutions. Only the initial segment of the curves in Figures 14 and 15 could be justifiably approximated by a straight line, the later portions could at best be described by a rate constant which decreases with time in a complex manner. This kind of response is characteristic of reactions in a viscous media. Such difficulty in representing the conversion data with the help of a simple kinetic scheme has been reported by Riggs and Rodriguez [177], and Ishige and Hamielec [178]. Both reported a first order dependence of the initial rate of reaction on monomer concentration in free radical initiated solution polymerization of acrylamide.
Figure 12. Fractional conversion vs. time of irradiation from $^{60}\text{Co}$ at 28°C for 1, 2 and 3% acrylamide.

Tables A-1, 3, 4
- 1% ACRYLAMIDE
- 2%
- 3%
Figure 14. \(-\ln(1-x)\) vs. \(t\) for 1, 2 and 3\% acrylamide under \(60^\circ\text{Co}\) at 28°C.

Tables A-1, 3, 4

\(1\%\) ACRYLAMIDE

\(2\%\)

\(3\%\)
Figure 15. $-\ln(1-x)$ vs. $t$ for 3% acrylamide in salt water under $^{60}\text{Co}$ at 28°C.
Ishige and Hamielec [178] used 'cage-effect' kinetic scheme (North, [179])—which takes into consideration the availability of the chain-initiating-free radicals being diffusion controlled—to explain the observed variation in the dependence of the reaction rate with monomer concentration. No satisfactory quantitative agreement was reached.

The situation in the present work was made more complicated by the fact that the dead times noticed in all reactions were dependent upon both initial monomer concentration and the salt content of the system. With the help of a simplified scheme for reactions in viscous media proposed in the next section, the \(-\ln(1-x) \text{ vs } \ln t\) straight lines were extrapolated to zero conversion \((x=0)\) and the intercepts on the time axis were taken as the dead times. These dead times in conjunction with first data points for each case were then used to determine the initial slopes of the curves. These values, which are also the overall rate constants, are shown in Table 1. Before these \(k_s\) could be compared with each other, however, it must be kept in mind that because of the dose rate variations in the horizontal plane, the samples were exposed to different dose rates. The time axis on all the graphs was generated on the assumption that all samples received a standard dose rate of 372 rads/min. Thus if the samples received a standard dose rate \(I_s\) for a time \(t_s\) then
TABLE 1

RATE CONSTANTS AND INDUCTION PERIODS AT 28°C AND 81°C

<table>
<thead>
<tr>
<th>Temp.</th>
<th>Monomer Concentration</th>
<th>Salt Concentration</th>
<th>Induction period (min.)</th>
<th>$x10^2$ I rads/min.</th>
<th>$k_{\text{corr}} x10^2$ 1st order</th>
<th>Density of solution (g/ml.)</th>
<th>$(k_p/k_t)^2$ $1^2 \text{sec}^{-1} \text{mole}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>28°C</td>
<td>1%</td>
<td></td>
<td>99</td>
<td>.76</td>
<td>385</td>
<td>0.77</td>
<td>1.01</td>
</tr>
<tr>
<td></td>
<td>2%</td>
<td></td>
<td>83</td>
<td>.88</td>
<td>353</td>
<td>0.85</td>
<td>1.02</td>
</tr>
<tr>
<td></td>
<td>3%</td>
<td></td>
<td>62</td>
<td>.81</td>
<td>394</td>
<td>0.83</td>
<td>1.03</td>
</tr>
<tr>
<td></td>
<td>5%</td>
<td></td>
<td>54</td>
<td>1.74</td>
<td>350</td>
<td>1.7</td>
<td>1.08</td>
</tr>
<tr>
<td></td>
<td>10%</td>
<td></td>
<td>33</td>
<td>1.99</td>
<td>355</td>
<td>1.9</td>
<td>1.13</td>
</tr>
<tr>
<td>81.5°C</td>
<td>3%</td>
<td></td>
<td>9</td>
<td>2.05</td>
<td>394</td>
<td>2.1</td>
<td>1.03</td>
</tr>
<tr>
<td></td>
<td>5%</td>
<td></td>
<td>20</td>
<td>3.27</td>
<td>350</td>
<td>3.2</td>
<td>1.08</td>
</tr>
<tr>
<td></td>
<td>10%</td>
<td></td>
<td>25</td>
<td>4.72</td>
<td>355</td>
<td>4.7</td>
<td>1.13</td>
</tr>
</tbody>
</table>
and the overall rate constant will be

\[ k_s = \frac{k_p}{k_t} (G_i I_s)^{\frac{1}{2}} \]  

(26)

But for a sample which was actually exposed to \( I \) rads/min. for \( t \) min.

\[ - \frac{d[M]}{dt} = \frac{k_p}{k_t} (G_i I)^{\frac{1}{2}}[M] \]  

(27)

Since the total dose absorbed is the same in the two cases

\[ I t = I_s t_s \]

or

\[ t = \frac{I_s}{I} t_s \]

upon substituting in equation (27)

\[ - \frac{I d[M]}{I_s dt_s} = \frac{k_p}{k_t} G_i^{\frac{1}{2}} I_s^{\frac{1}{2}}[M] \]

\[ - \frac{d[M]}{dt_s} = \frac{k_p}{k_t} G_i^{\frac{1}{2}} \frac{I_s}{I}\frac{I_s}{I_s}[M] \]

or

\[ -\ln(1-x) = \frac{k_p}{k_t} G_i^{\frac{1}{2}} \frac{I_s}{I}\frac{I_s}{I} (t_s-t_i) \]

i.e., a plot of \(-\ln(1-x)\) vs \( t_s \) will yield an overall rate constant equal to \( \frac{k_p}{k_t} G_i^{\frac{1}{2}} \frac{I_s}{I}\frac{I_s}{I} \), but since we are interested in comparisons under standard conditions of \( I_s \) and \( t_s \), where the overall rate constant is only \( \frac{k_p}{k_t} G_i I_s^{\frac{1}{2}} \); we must
multiply the slopes obtained from the graphs by \( \frac{I_1^k}{I_S^k} \) to get the corrected value of the overall rate constant \( k_s \). The author believes that lack of application of this correction factor was what prompted Collinson et al., [128] to comment "Generally results obtained from experiments with different monomer concentrations but a constant dose rate are consistent; those from experiments at different dose rates never are."

The corrected \( k \) values are also shown in Table 1. A further correction that could be applied would be consideration of the difference in electron density, but as shown in Appendix C and discussed earlier it is negligible.

It is seen from the values of \( k_s \) that the presence of small quantities of salt significantly increased the rate of reaction while the increase with additional quantities was marginal. Values of \( \frac{k_p}{k_t^{1/2}} \) calculated from \( k_s \) (equation 26), assuming \( G_1=8.2 \) (i.e., 8.2 free radicals formed per 100 ev absorbed), are also tabulated in Table 1. An average value of \( \frac{k_p}{k_t^{1/2}} = 0.59 \text{ l}^{1/2}/\text{mole}^{1/2}-\text{sec}^{1/2} \) is to be compared with \( 4.7 \text{ l}^{1/2}/\text{mole}^{1/2}-\text{sec}^{1/2} \) as reported by Collinson et al., [128]. The low value obtained in this study could be partly due to impurities in the system (no attempts to purify the monomer were made) which would increase the rate of chain termination, and partly due to incomplete deoxygenation which would reduce the rate of polymerization. Moreover, no special efforts were made to measure the initial rate of reaction in this study.
A4. A Simplified Scheme for Reactions in Viscous Media

Apart from the advantages of having a general expression to fit a data set, the need for devising a model for the extent of reaction in a viscous media was twofold. One, to extrapolate the $-\ln(1-x)$ vs $t$ data, discussed in the previous section, to zero conversions with reasonable accuracy; and two, to formulate an expression for the relationship between the total dose absorbed and the degree of conversion. This expression will be useful later in predicting the extent of reaction in the case of reactions run with dissolved $^{32}$P.

Despite the fact that they hold true for only small particles, the two popular models: (1) the Rabinowich model [180] and its modified form, 'volume swept out' model and (2) the Smoluchowski model (Noyes, [181]) could not be employed because of the lack of diffusivity data and also because of the complexity of the latter.

Chemical reactions in viscous media proceed through three different regions (Allen and Patrick, [69]): (1) kinetic region, where the reaction essentially follows a first order kinetics based on monomer concentration and square root dependence on the rate of initiation; (2) auto acceleration region, also known as gel effect or Trommsdorf effect, which takes over when the medium becomes somewhat viscous, and the diffusivity of the macro-radicals is severely limited. Unless other rate
coefficients change, the rate of polymerization increases with conversion; (3) at higher conversions, and therefore higher viscosities (slight crosslinking may also occur under suitable conditions), diffusion of even the monomer is restricted, causing the rate of reaction to slow down. A typical $x$ and $R_p$ vs. $t$ curve for such a reaction is shown in Figure 16.

The gel effect region is not yet well understood and the high conversion region is rarely sufficiently well studied (Allen and Patrick, [69]).

The proposed scheme assumes that the rate of reaction and the distribution of the initiating species are uniform throughout the medium. Such is almost always the case with radiation induced reactions. Under these conditions in the gel effect region and beyond, it can be said that the differential change in the monomer concentration per unit absorbed dose will be proportional to the monomer concentration

$$- \frac{d[M]}{dD} \propto [M]$$

Also, since the medium has become so viscous as to significantly hinder the diffusion of species in the solution, more and more dosage is required to cause the same change in the monomer concentration. In other words, the higher the total dose already received, the less will be the change per unit dose.

$$- \frac{d[M]}{dD} \propto \frac{1}{D}$$
Figure 16. Typical rate and extent of reaction vs. time for reactions in viscous media.
Combining the two,

$$- \frac{d[M]}{dD} \propto \frac{[M]}{D}$$

or

$$- \frac{d[M]}{dD} = S \frac{[M]}{D}$$

where $S$ is the constant of proportionality. Upon integrating from $(D_0, M_0)$ to $(D, M)$, we get

$$- \ln \left( \frac{M}{M_0} \right) = S \ln D - S \ln D_0$$

where $D_0$ is the dose needed to establish a stationary concentration of free radicals (analogous to dead time) or

$$-\ln(1-x) = S \ln D - S \ln D_0 \quad (28)$$

i.e., a plot of $\ln(1-x)$ vs $\ln D$ should be a straight line.

Two cases are possible:

(I) In the case of constant dose rate:

$$D = It;$$

therefore, we can also write,

$$-\ln(1-x) = S \ln t - S \ln t_0 \quad (29)$$

A plot of $-\ln(1-x)$ vs $\ln t$ will be a straight line.

(II) In the case where the intensity of irradiation is decaying exponentially:

$$I = I_0 e^{-\lambda t}$$

Then, the total dose received by the sample in a time $t$ is given by
\[ D = \int_{t_o}^{t} I_o e^{-\lambda t} dt \]

\[ D = I_o \frac{(1-e^{-\lambda t})}{\lambda} \]

and

\[ dD = I_o e^{-\lambda t} dt \]

Substituting for \( D \) and \( dD \) in the proposed expression

\[ \frac{d[M]}{dD} = S \frac{[M]}{D} \]

\[ \frac{d[M]}{I_o e^{-\lambda t} dt} = S \frac{[M]}{I_o \frac{(1-e^{-\lambda t})}{\lambda}} \]

\[ \frac{d[M]}{[M]} = S \frac{e^{-\lambda t} dt}{(1-e^{-\lambda t})} \]

Integrating with the boundary condition that at \( t = t_o \), \( M = M_o \), we obtain

\[ \ln \frac{[M]}{[M]_o} = S \ln \frac{(1-e^{-\lambda t})}{(1-e^{-\lambda t_o})} \]

or

\[ -\ln(1-x) = S \ln \frac{(1-e^{-\lambda t})}{(1-e^{-\lambda t_o})} \]

where \( t_o \) can be found from

\[ D_o = \frac{I_o}{\lambda} (1-e^{-\lambda t_o}) \]

if \( D_o \) is known.
The above expression can also be written as

\[-\ln(1-x) = S \ln \frac{I_0/\lambda (1-e^{-\lambda t})}{I_0/\lambda (1-e^{-\lambda t_0})}\]

which is nothing but

\[-\ln(1-x) = S \ln \frac{D}{D_0}\]

the same expression for the case with constant dose rate.

It indicates that the \(-\ln(1-x) vs \ln D\) plots are comparable not only for the cases where the samples were exposed to unequal dose rates but also where these dose rates were decaying exponentially. This is unlike the case with the usual \(\ln(1-x) vs t\) plot derived from

\[-\frac{d[M]}{dt} = k[I]^n[M]\]

where clearly both the magnitude and decay rate of \([I]\) will influence the experimental determination of \(k\).

\(-\ln(1-x) vs \ln t\) plots for 1, 2 and 3% monomer solutions at 28°C and 3% monomer solution containing 0, 5 and 10% salt at both 28°C and 80°C are presented in Figures 17, 18 and 23. Excellent linear fits were obtained with the values of the correlation coefficient ranging from 0.9989 to 0.9455. While making a fit, in some cases the last data point was discarded. It was felt that the yield analysis on these were not reasonably accurate because some monomer trapped inside the crosslinked gel might not have been accounted for.
Tables A-1, 3, 4

- $1\%$ ACRYLAMIDE
- $2\%$
- $3\%$

Figure 17. $-\ln(1-x)$ vs. $\ln t$ for $1\%$, $2\%$, $3\%$ acrylamide solutions under $^{60}$Co at $28^\circ C$. 

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Figure 18. \(-\ln(1-x)\) vs. \(\ln t\) for 3% acrylamide solutions in salt water under \(^{60}\text{Co}\) at 28°C.
Three peculiar features of expressions (28) and (29) are noteworthy. First, they predict that a 100% conversion is never achieved, since the viscosity also increases along with it. Second, there must be some dead time in the system -- no matter how small, before a uniform and stationary concentration of the free radicals can be achieved. Third, straight lines with higher initial monomer concentrations have smaller slopes than those corresponding to lower initial monomer concentration. This is because -- for the same extent of reaction -- the viscosity of the solution with higher initial monomer concentration will be more and therefore its rate of reaction less than those in the solution initially containing less monomer. In order to gain more insight into the nature of the slope and the intercept of the straight lines, let us interpret the reaction from the standpoint of the conventional kinetics. Let us say that \( n \) is the time averaged order of the reaction and since reactions in viscous media are inherently slow (especially after the monomer concentration has depleted significantly), \( n > 1 \). The rate of such a reaction could be written as:

\[
-\frac{d[M]}{dt} = k[M]^n
\]  

(30)

If the initial monomer concentration is \([M_0]\), then

\[
-[M_0] \frac{d([M]/[M_0])}{dt} = k[M_0]^n \left(\frac{[M]}{[M_0]}\right)^n
\]
or

\[- \frac{d\left(\frac{[M]/[M_0]}{([M]/[M_0])^n}\right)}{([M]/[M_0])^n} = k [M_0]^{n-1} \, dt\]

Integrating from \(t = t^0\) where \([M] = [M_0]\) to \(t = t^1\)

\[- \frac{([M]/[M_0])^{1-n}}{1-n} \left. \frac{[M]}{[M_0]} \right|_{[M_0]} = k [M_0]^{n-1} (t - t^0) \quad n \neq 1\]

or

\[- \left(\frac{[M]}{[M_0]}\right)^{1-n} + 1 = k [M_0]^{n-1} (1-n) (t-t^0)\]

when the reaction has advanced far enough \([M] \ll [M_0]\) and actually, in the case of reactions in viscous media such a situation may arise quite early in the course of reaction because of the pseudo reduction in the local concentration of the monomer. Under such conditions \([M_0]/[M] \gg 1\), and since \((n-1) > 0\)

\[- \left(\frac{[M_0]}{[M]}\right)^{n-1} - 1 = k (n-1) [M_0]^{n-1} (t-t^0)\]

or

\[- \ln \left(\frac{[M_0]}{[M]}\right)^{n-1} = k (n-1) [M_0]^{n-1} (t-t^0)\]

or

\[- \ln [M_0]/[M] = \ln k (n-1) [M_0]^{n-1} + \ln(t-t^0).\]

\[- \ln \left(\frac{[M_0]}{[M]}\right) = \frac{1}{(n-1)} \lnk (n-1) [M_0]^{n-1} + \frac{1}{(n-1)} \ln(t-t^0)\]
\[ -\ln(1-x) = \frac{1}{(n-1)} \ln t + \frac{1}{(n-1)} \ln k(n-1)[M_o]^{n-1} + \frac{1}{(n-1)} \ln(1-t_o/t) \]

For \( t >> t_o \) the last term can be neglected, at least for a first approximation. Substituting

\[ x = 1 - \left[ \frac{M}{M_o} \right] \]

we obtain the final expression

\[ -\ln(1-x) = \frac{1}{(n-1)} \ln t + \frac{1}{(n-1)} \ln k(n-1)[M_o]^{n-1} \]

(31)

i.e., a plot of \(-\ln(1-x)\) vs \(\ln t\) will have a slope of \(1/(n-1)\) and an intercept \(\frac{1}{(n-1)} \ln k(n-1)M_o^{n-1}\). It can be seen from the above expression that since larger values of \(n\) will be associated with slower reactions in media of higher viscosity because of higher initial monomer concentration, the slope of \(-\ln(1-x)\) vs \(\ln t\) lines will be smaller than their counterparts with lower initial monomer concentration. Equation (31) is unusual in the sense that the rate constant appears in the intercept of the line.

As mentioned earlier, the \(-\ln(1-x)\) vs \(\ln t\) plot showed an excellent fit for the data obtained in the present study. It would be appropriate to check the validity of this method by applying it to the data reported elsewhere. Unfortunately, conversion-time data on reactions in viscous media for conversions up to ~1.0 are extremely rare. Rate constants are usually determined by assuming a first order reaction up to 20-30% conversion, and this
is also the range of the reported x-t data. Data on reactions in precipitating media cannot be used for obvious reasons. The data used here were obtained from a study of the bulk polymerization of methyl methacrylate (Hayden and Melville, [182]). Unfortunately, the values of the rates of reaction $R_p$ at corresponding conversions $x$ were reported and not the x-t data. Although a plot of $R_p$ vs $x$ exhibited the expected behavior in the gel effect region and the region beyond it where $R_p$ was controlled by monomer diffusion, it was not possible to determine the initial time from the reported values. The $R_p$ vs $x$ curve was then approximated by a parabola for $x > 0.45$.

$$R_p = 1.5951x^2+1.3796x-0.0528$$

Since

$$R_p = -\frac{dM}{dt} = M_0 \frac{dx}{dt}$$

we can obtain an expression relating $x$ and $t$ by integrating the expression for $R_p$.

$$0.7990 \ln \left[ \frac{x-0.0402}{1.0934(0.8248-x)} \right] = \frac{t}{M_o} - \frac{t_{0.45}}{M_o}$$

It was not possible to determine the time taken for conversion to reach 0.45. It was therefore arbitrarily set equal to 300 $M_o$ min. Values of $t/M_o$ corresponding to given $x$ were calculated and plotted in the form of $-\ln(1-x)$ vs $\ln t$ (Table 2 and Figure 19). The correlation coefficient

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TABLE 2

TREATMENT OF DATA OF HAYDEN AND MELVILLE (1967) ON BULK POLYMERIZATION OF METHYLMETHACRYLATE

Equation used to fit the data

\[ R_p = 1.5951 x^2 + 1.3796x - 0.0528 \text{ where } x > 0.45 \]

or

\[ 60 \times 0.7990 \ln \left[ \frac{x-0.0402}{1.0934 (0.8248-x)} \right] = \frac{t}{M_o} - \frac{t_{0.45}}{M_o} \]

where \( t \) is in min. and \( \frac{t_{0.45}}{M_o} = 300 \) (arbitrarily)

<table>
<thead>
<tr>
<th>( x )</th>
<th>( R_p ) (hr(^{-1})) reported</th>
<th>( R_p ) (hr(^{-1})) calcu.</th>
<th>( \frac{t}{M_o} )</th>
<th>-( \ln(1-x) )</th>
<th>( \ln(\frac{t}{M_o}) )</th>
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<tr>
<td>0.45</td>
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<td>24.5</td>
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<td>0.598</td>
<td>5.704</td>
</tr>
<tr>
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<td>0.693</td>
<td>5.744</td>
</tr>
<tr>
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<td>22.5</td>
<td>22.3</td>
<td>325</td>
<td>0.799</td>
<td>5.785</td>
</tr>
<tr>
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<td>20.0</td>
<td>20.1</td>
<td>340</td>
<td>0.916</td>
<td>5.874</td>
</tr>
<tr>
<td>0.65</td>
<td>17.0</td>
<td>17.0</td>
<td>356</td>
<td>1.050</td>
<td>5.874</td>
</tr>
<tr>
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</tr>
<tr>
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<td>404</td>
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<td>6.000</td>
</tr>
<tr>
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<td>3.0</td>
<td>3.0</td>
<td>460</td>
<td>1.609</td>
<td>6.131</td>
</tr>
</tbody>
</table>

-\( \ln(1-x) \) vs. \( \ln(\frac{t}{M_o}) \) fitted with a straight line

\[ -\ln(1-x) = 2.701 \ln \left( \frac{t}{M_o} \right) - 14.82 \]

with a correlation coefficient of 0.994.

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Figure 19. Linearization of data of Hayden and Melville [182] under the proposed scheme.
in this case was 0.994. Such a high degree of correlation lends some confidence to the proposed method of treatment of data.

A5. Effect of Salt on the Reaction

The presence of salt increased the rate of reaction greatly (Table 1). At the same time it seemed to delay the onset of macromolecular entanglement. At present, there is no satisfactory explanation that could account for the increased rate of reaction. The possibility that the presence of salt increases the equilibrium concentration of free radicals in the solution could explain two of the observed phenomena: (1) higher rates of reaction and (2) higher conversions necessary to ensure macromolecular entanglement at increased salinity (because higher free radical concentration would generate shorter polymer chains). However, in the absence of any reasonable mechanism to account for higher free radical density in the presence of salt, the credibility of this theory is questionable. As reported by Allen (Ref. 174, p. 108) -- irradiation of bromide and iodide solutions failed to show any significant build up of free Br\(_2\) and I\(_2\) -- it is unlikely that Cl\(\cdot\) radicals would be a stable species in saline solutions. The only statement that can be made with certainty at present is that acrylamide is a better free radical scavenger in the presence of salt, and this causes a higher rate of reaction.
The decrease in the hydrodynamic volume of the polymer formed in salt solutions can be approached in an interesting manner. As mentioned earlier in the theory of reptating macromolecules, a critical concentration of macromolecules of a given DP is needed before crosslinking may begin. Schurtz and Hochberger [183] concluded from their experiments on polyisobutylene in toluene, that

$$N_C = \text{constant } C^{-1.28}$$

[Klein] 124 derived from theoretical considerations

$$N_C = 65C^{-1.25}$$

for the above system. In the absence of any data on polyacrylamide, we will use the above equation to get a rough estimate of the hydrodynamic volume of the chains. (Although in reality, it is expected that because of the polar nature of amide groups, chain-chain interactions in polyacrylamide macromolecules would occur at a lower chain length than that calculated from the above equation for non-polar polyisobutylene). Also, the radius of gyration $$<s^2>^{1/2}$$ of a freely jointed chain of $$N_C$$ segment of unit length $$l$$ is given by (C.f., Ref. 192):

$$<s^2>^{1/2} = \left( \frac{N_C l}{6} \right)^{1/2}$$

In the case of acrylamide $$l = 2.51\,\text{A}^0$$, and then

$$<s^2>^{1/2} = 5.21\,C^{-0.63}$$

(32)
Thus the radii of gyration in the cases of 3% acrylamide in 0, 5 and 10% salt solutions, where the conversions needed for the onset of entanglement were 0.63, 0.73 and 0.86 respectively (Figure 10); can be calculated from equation (32) to be 63.5 A°, 57.9 A° and 52.2 A° respectively. The minimum radius of gyration of a macromolecule necessary to ensure crosslinking in a 3% solution can be also calculated as 47.5 A°. This corresponds to a DP of ~5400.
B. Irradiation of Acrylamide Solutions at 80°C with $^{60}\text{Co}$

For reasons discussed earlier, the radiation induced reactions at high temperature were run with 3% monomer solutions containing 0, 5 and 10% salt. For comparison purposes persulfate initiated free radical polymerizations of 1, 2 and 3% acrylamide in 0.5 and 10% salt solution were also run at 80°C. The reactant composition in these reactions was proportional to that suggested by Sorenson and Campbell ([134], p. 248). The relative viscosity vs. time response of all of the above experiments at high temperature are compared with those at room temperature in the following pages.

Bl. Effect of Temperature on the Reaction

The relative viscosity of the solution and the extent of conversion as functions of dose are shown in Figures 20 and 21 respectively. Once again points on the $-\ln(1-x)$ vs. $t$ plot (Figure 22), did not fall on a straight line, but on a $-\ln(1-x)$ vs. $\ln t$ plot (Figure 23), they did. The values of the induction periods were found after extrapolating these lines to $x=0$, and then based on these induction periods the magnitudes of the first order rate constants were calculated as the slopes of the straight lines approximating the initial portions of $-\ln(1-x)$ vs. $t$ data. The values of $k$ were then corrected for
Figure 20. Relative viscosity of 3% acrylamide in salt water vs. dose from $^{60}$Co at 81.5°C. (Fractions denote fractional conversions at those points).
Figure 21. Fractional conversion vs. time of irradiation under $^{60}$Co at 81.5°C for 3% acrylamide in salt water.
Figure 22. \(-\ln(1-x)\) vs. \(t\) for 3% acrylamide in salt water under \(60_{\text{Co}}\) at 81.5°C.
Figure 23. $-\ln(1-x)$ vs. $\ln t$ for 3% acrylamide in salt water under $^{60}\text{Co}$ at 81.5°C.
differences in dose rates as explained earlier. These, along with the calculated values of the induction period are shown in Table 1. The increase in the overall rate constant was not remarkable although significant reduction in the induction periods was noticed. A few striking differences in the behavior of the polymerizing solutions at the two temperatures were brought out by the comparison of Figures 10 and 20. The most important one was that while the polymers formed in the solutions at room temperature sooner or later proceeded to crosslink, the viscosities of the solutions at 80°C first increased and then continually decreased indicating degradation of polymer. Closer examination revealed that the rate of increase of viscosity at higher temperature was lower than that at lower temperature, while the rate of reaction at high temperature was faster than that at the lower temperature. It appears, therefore, that the ratio of the rate of chain formation to chain scission per 100 ev absorbed, a/β was < 1 and that depolymerization sets in almost from the beginning. Essentially oligomers would be formed under these conditions. As calculated in the last section, the minimum degree of polymerization essential for molecular entanglement in the case of 3% monomer solution was ~5400. It can, therefore, be said that correspondingly more macromolecules of DP < 5400 were formed at 80°. Since the rate of free radical generation in
water under irradiation at constant dose is relatively independent of temperature, it can be concluded that the free radical scavanging efficiency of acrylamide increases with temperature. Furthermore, since the relative viscosity of the solution exposed to radiation at 80°C decreased continually after reaching a maximum (Figure 20) while the relative viscosity of the persulfate initiated polymerization at 80° (Figure 24) decreased little even though kept at 80° for a longer time than the former -- it could be deduced that it is the process of irradiation that adversely affected the polymer at 80°C. If at the completion of reaction (or in the case of a dynamic process, somewhere near the completion) the DP of the polymers formed were less than \( N_c \), the free radicals, which were being continuously generated in the surrounding medium exposed to constant irradiation, would attack these oligomers. The fragments would not recombine immediately because of their sluggishness and further radical attack would cause further scission. As a result, the solution viscosity continued decreasing. Following this logic, it can be seen that the equilibrium viscosity of the solutions would correspond to that DP where the probability of recombination of the macroradicals (a function of their size and number density) is balanced by the frequency of the free radical attack on them (a function of dose rate and salt concentration).
Figure 24. Relative viscosity vs. time of reaction for persulfate initiated polymerization of 1, 2 and 3% acrylamide in 0, 5 and 10% salt solutions at 80°C.

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The first order rate constants increased by approximately a factor of two for an increase in temperature of more than 50°C. Such low increases in the rate constants are typical of radiation induced reactions, which are characterized by low activation energies.

B2. Effect of Salt on the Reaction

The first order rate constant increased by a factor of two from that in the salt free solution to that in the 10% saline solution (Table 1). This relative increase was unaffected by the increase in temperature. Also, the initial rate of increase of viscosity was higher in the solutions with higher concentration of salt. Again, as argued earlier, the presence of increasing amounts of salt caused the hydrodynamic volume of the polymer to decrease. According to a rough estimate made later in this report, the intrinsic viscosity of the 3% monomer in 10% salt was calculated to be 2.25. Using $[\eta]$ vs. $[\overline{M}_\eta]$ relationship (equation 13), the DP of the polymer was evaluated to be ~3000. This DP is much lower than that necessary for entanglement (c.f. 5400).

When the response of radiation polymerized 3% acrylamide at 80°C (Figure 20) is compared with that of $K_2S_2O_8$ initiated polymerization also at 80°C (Figure 24), another striking difference is noticeable. The presence of salt in chemical polymerization drastically reduced the solution
viscosity and also affected the rate of viscosity increase adversely. One possible explanation could be that the presence of salt may promote monomer chain transfer (resulting in lower viscosity) and the chain reinitiation is slow (resulting in slower overall rate of reaction).

B3. Calculation of the Activation Energy

Using the rate constants obtained at the two temperatures (28°C and 81.5°C) and various salt concentrations the activation energy can be calculated as

$$\Delta E = \frac{d \ln k}{d (1/T)}$$

These values are tabulated in Table 3. From the data it is difficult to tell if the presence of salt has any influence on the activation energy. An average value of $\Delta E$, therefore, was calculated to be 3.2 Kcal/mole. The value reported in the literature [128], calculated also between two points (25° and 45°) is 1.5 Kcal/mole. The discrepancy between the two values could be attributed to the not so rigorous temperature control and the degree of uncertainty involved in the estimates of the induction periods on which the $k$ values were based in this experiment.
TABLE 3

CALCULATION OF ACTIVATION ENERGY

ln k values for 3% monomer.

<table>
<thead>
<tr>
<th>T°C</th>
<th>$1/\text{T}^\circ \text{K}$</th>
<th>Salt</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0%</td>
</tr>
<tr>
<td>28°</td>
<td>$3.320 \times 10^{-3}$</td>
<td>-4.788</td>
</tr>
<tr>
<td>81.5°</td>
<td>$2.820 \times 10^{-3}$</td>
<td>-3.857</td>
</tr>
<tr>
<td>ΔE Kcal/mole</td>
<td>3.700</td>
<td>2.512</td>
</tr>
</tbody>
</table>

$\Delta E_{av} = 3.21 \text{ Kcal/mole}$
C. Irradiation of Acrylamide Solutions in Capillaries at 80°C with Dissolved $^{32}$P

The relative viscosities of the solutions (3% acrylamide in 10% w/v salt) inside different diameter tubes as a function of total apparent dose is shown in Figure 25. The total apparent dose is defined as the dose which the solutions in the tubes would have received if they could absorb all of the emitted radiation. Although the solutions did not crosslink (on the contrary, they decreased in viscosity after a certain maximum was reached), distinctly increasing rates of increase of solution viscosity were observed as the diameter of the capillaries increased. These and other observed phenomena are discussed in the following sections, and compared with the predictions made from fundamental considerations of efficiency of energy transfer.

It should be mentioned at this point that since the densities of the monomer solution (-1.13 gm./cm.$^3$), the tube walls (-0.98 gm./cm.$^3$), and the surrounding medium (-1.1 gm./cm.$^3$) are very nearly the same, the 'wall-effect' -- scattering of $\beta$ particles as they enter a medium of different density -- is not considered to be important in this case. Also, since the average and maximum depths of penetration of $\beta$ particles emitted by $^{32}$P in water are 0.25 and 0.79 cm. respectively, a spacing of 0.6 cm. between the segments of the tubes appeared to be sufficient
Figure 25. Relative viscosities of the solutions -- in different diameter capillaries containing dissolve $^{32}$P vs. total apparent dose.
to keep to a minimum one segment of the tube from being affected by the β particles from another segment.

Cl. **Derivation of the Relationship between the Total Dose Absorbed and the Relative Viscosity of the Solution**

The purpose of the experiments conducted with the radioactive source dissolved in the solutions in different diameter capillaries was to demonstrate that the extent of polymerization at any time will be a function of the diameter of the capillary. Since only viscosity vs. time data were obtained in these experiments (and presented as relative viscosity vs. total apparent dose absorbed in Table A-12 and Figure 25 it was necessary to somehow predict and/or correlate the extent of reaction from the viscosity of the solution. Direct use of the relative viscosity vs. total dose absorbed data from the $^{60}$Co experiments at 80°C was not possible because of two facts. First, the dose rates in the two cases are very different; a steady 372 rads/min. in the case of $^{60}$Co, and an exponentially decaying dose rate of initial strength 22 rads/min. in the case of $^{32}$P. This makes the comparative time scales in the two cases extremely complicated. Second, polymer degradation was observed in both cases, and since it was not possible to separate the dose rate effect from the time effect on depolymerization, the viscosity vs. dose correlations
cannot be validly transplanted from one case into the other. Efforts were therefore made to predict only the polymerizing portions of the response, and in doing so a few clues were taken from the $^{60}$Co experiments.

The time vs. conversion data in the case of $^{60}$Co experiments with 3% monomer and 10% salt solutions at $80^\circ$C was calculated to be, after linearization, (Figure 23, Table A-9)

$$-\ln(1-x) = 1.66 \ln t_s - 5.33$$

where $t_s$ was the time with the assumption of a constant dose rate of 372 rads/min. Since reactions proceed according to the number of free radicals generated, which is directly proportional to the total dose absorbed, the above equation should be applicable to the $^{32}$P case if the time is converted into dose. Again, since

$$D = 372 t_s \text{ rads}$$

$$-\ln(1-x) = 1.66 \ln D - 15.16 \quad (33)$$

Now, if the effective cross section for absorption of the total emitted radiation for a tube of radius $a$ is $\phi_a$; then the tube would have intercepted a total dose of $\phi_a D \text{ rads}$, when the total emitted (apparent) dose is $D$. Therefore, to generalize the above equation for capillaries of different diameter, it should be written as:

$$-\ln(1-x) = 1.66 \ln \phi_a D - 15.16 \quad (34)$$
Values of $\phi_a$ for cylinders of different radii are calculated in the next section.

Now, there are two most commonly used methods of determination of intrinsic viscosity of a polymer. These are derived from, one, due to Huggins [185]

$$\frac{\eta_{sp}}{C} = [\eta] + k'[\eta]^2C$$

(35)

and the other one due to Kramer [186]

$$\frac{1}{C} \ln \eta_r = [\eta] + k''[\eta]^2C$$

(36)

where $k'$ and $k''$ are constants for the polymer solvent system such that (Billmeyer, [187])

$$k' - k'' = 0.5$$

(37)

The fact that for a given concentration of polymer the two equations must give the same values of viscosity and hence $\eta_r$ and $\eta_{sp}$, can now be used to calculate the unknowns $(k', k'', [\eta])$ in the equations (35), (36) and (37). We know that if the extent of reaction is $x$ in a monomer solution initially containing 3 g./dl., the concentration of polymer in g./dl. of the solution is,

$$C = 3x$$

Substituting for $k'$ from (37) and using the fact that

$$\eta_{sp} = \eta_r^{-1}$$

by definition, it can be seen that

$$\eta_r = 1 + 3[\eta]x + 9(k''+0.5)[\eta]^2x^2$$

(38)
\ln \eta_r = 3[\eta]x + 9k"[\eta]^2x^2 \quad (39)

Now, the maximum relative viscosity attained in the high temperature experiments on 3\% monomer with 10\% using $^{60}\text{Co}$ was \( \sim 27 \). Assuming that at this point the monomer was almost all converted into polymer \((x=1.0)\), we get from (38) and (39)

\[ 27 = 1 + 3[\eta] + 9(k"+0.5)[\eta]^2 \]

\[ \ln 27 = 3[\eta] + 9k"[\eta]^2 \]

solving for \( \eta \) and \( k" \), we get

\[ \eta = 2.25 \text{ dl./g.} \]
\[ k" = -0.076 \]
\[ k' = 0.424 \]

This value of \([\eta]\) corresponds to, as shown earlier, a molecular weight which is much less than that needed for crosslinking. Substituting the values obtained above in (38), we obtain an expression for the relative viscosity of the solution as a function of the extent of reaction

\[ \eta_r = 1 + 6.74 x + 19.26 x^2 \quad (40) \]

This can also be seen as a power series dependence of \( \eta_r \) on \( x \), the series truncated after the third term. Thus we have a set of equations expressing the relative viscosity of the solution as a function of the total rads absorbed:

\[ \eta_r = 1 + 6.74 x + 19.26 x^2 \quad (40) \]
and
\[ x = 1 - \exp\{-1.66 \ln D_a - 15.16\} \]  
(c.f. eqn. 34)

where the total dose \( D \) can be calculated from
\[ D = 6.464 \times 10^5 (1 - e^{-3.385 \times 10^{-5} t}) \]  
(20)

\( t \) is in minutes. Equations (40), (34), (20) can be used to calculate the relative viscosity of the solution after \( t \) minutes of irradiation with dissolved \(^{32}\)P.

C2. Mathematical Derivation of the Fraction of Total Emitted Radiation Absorbed by the Cylinder Containing Radioactive Fluid

As mentioned previously, the dose received by a point inside the cylinder will be a function of its location inside the cylinder, the number density, and the distance of the sources from this point and among other things, the attenuation coefficient for the medium. Throughout the rest of the section, the medium has been assumed to be of unit density. Thus, the distances in \( \text{gm./cm.}^2 \) are numerically equal to those in cm.

Appendix D shows the calculations for the area \( S \) of a spherical shell which will be contained inside a cylinder. The generalized result is presented below.

\[ S = 4R^2 \left\{ \pi - \int_0^{\pi/2} \sqrt{1 - \left( \frac{r_c}{R} \right)^2} \, d\theta \right\} \]  
(41)
where
\[ r_c = \sqrt{a^2 - b^2 \cos^2 \theta - b \sin \theta} \]  \hspace{1cm} (42)

and \( \theta_x \) for various values of \( R, a \) and \( b \) is

<table>
<thead>
<tr>
<th>R&lt;(a-b)</th>
<th>(a-b)&lt;R&lt;(a+b)</th>
<th>R&gt;(a+b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>b=0</td>
<td>( \pi/2 )</td>
<td>--</td>
</tr>
<tr>
<td>b&lt;a</td>
<td>( \pi/2 )</td>
<td>( \sin^{-1} \left( \frac{a^2 - b^2 - R^2}{2br} \right) )</td>
</tr>
<tr>
<td>b=a</td>
<td>--</td>
<td>( \sin^{-1} \left( \frac{a^2 - b^2 - R^2}{2br} \right) )</td>
</tr>
</tbody>
</table>

The different variables in these equations are explained in Figure 26. Now, the modified point source expression of Loevinger (1952) is

\[ D(R) = \frac{K}{(\nu R)^2} \left[ C - \frac{\nu R}{C} e^{1-\nu R/C} \right] + \nu R e^{1-\nu R/C} - \nu R e^{1-\nu R_m} \]

\[ [1- \frac{\nu R}{C} e^{1-\nu R/C}] = 0 \text{ for } \nu R/C > 1. \]  \hspace{1cm} (14)

where the significance of the terms has been explained earlier. For \( ^{32}P \),

\[ C = 1 \]

\[ R_m = 0.79 \text{ gm./cm.}^2 \]

\[ \nu = 9.18 \text{ cm.}^2/\text{gm.} \]

The value of \( K \) was calculated from the following equation:
Figure 26. Significance of the variables involved in the calculation of surface area of a sphere contained inside a cylinder.
\[ K = 169.87 \bar{E} v^3 / \{3-(1-v)R_m e^{1-vR_m} - v^2 R_m^2 e^{1-vR_m}\} \]

\[ = 31759 \text{ rads/hr-millicurie} \]

The variation of \( D(R) \) as a function of \( R \) for \( ^{32}\)P in water is shown in Figure 27.

If the concentration of such sources in the fluid is given by \( C_v \) millicuries/ml., then the dose received by a point from the sources located in a thin spherical shell of radius \( R \) in a medium of unit density is, from equations (41) and (14)

\[
4\pi/2 \left\{ \sqrt{1-(r/R)^2} \int_{\theta} \right\} R^2 D(R) C_v dR \text{ rads/hr.}
\]

where the bracketed term takes into account that only that part of the shell that is inside the cylinder, contains radioactive sources. The total dose received by the point under consideration (which is, say, situated at a distance \( b \) from the center) from all the possible sources is given by the integral

\[
D_a(b) = 4 \int_{R=0}^{R_m} C_v \left\{ \pi/2 \left\{ \sqrt{1-(r/R)^2} \int_{\theta} \right\} R^2 D(R) dR \text{ rads/hr.} \right\}
\]

subject to the restrictions placed on \( \theta > \) which depend upon the relative magnitudes of \( a, b \) and \( R \), as \( R \) varies from 0 to \( R_m \). It is not possible to obtain an analytical solution for \( D_a(b) \). It was, therefore, numerically integrated using the composite Simpson's Rule (Conte and de Boore, [188]), the expression for which follows:
Figure 27. Fractional dose rate received by a point situated at a distance \( R \) from \(^{32}\text{P}\) point sources dissolved in water.
\[ S_N = \frac{h}{6} \left[ f_0 + f_N + 2 \sum_{i=1}^{N-1} f_i + 4 \sum_{i=1}^{N} f_{i-\frac{1}{2}} \right] \] (44)

where the total interval was divided into \( N \) divisions each of length \( h \). The value of the integrand at the \( i \)th point is \( f_i \) and \( f_{i-\frac{1}{2}} \) is the value of the integrand at half way between the \( i \)th and \((i-1)\)st point. The values of \( \Delta \theta \) and \( \Delta R \) used in the computer program were 2° and 0.01 respectively. It was found that the results did not vary significantly if these intervals were cut in half. The uncertainties involved in the experimental results ranged from 1-5%. An accuracy of about 0.001 in the case of the computed results was judged satisfactory.

The dose received by a point situated at a distance \( b \) from the cylinder axis as a fraction of that received at the axis is shown in Figure 28 for different diameter cylinders. Figure 29 depicts the fraction of total emitted dose absorbed by the points on the axes of cylinders of various diameters. Once the radius of the cylinder exceeds the maximum depth of penetration of radiation (0.79 cm.), the points on the axis cannot distinguish between the cylinder and an infinite reservoir. This fact is exhibited in that the fraction absorbed is 1.0 for cylinders of radii > 0.8 gm./cm.².

Now, to calculate the fraction of total dose absorbed by a cylinder of a given radius, we note that
Figure 28. Fraction of the axial dose rate received by a point inside a cylinder containing radioactive $^{32}$P water.
Figure 29. Axial dose rate (as fraction of total emitted dose) as a function of cylinder radius.
from the symmetry of the situation, all points situated at a distance $b$ from the axis receive the same intensity of dose. Then

$$\phi_a = \frac{\int_0^a 2\pi b D_a(b) db}{\pi a^2 \epsilon}$$

(45)

where $\epsilon$ is the total energy released per unit volume (in this work, it corresponds to 1 millicurie/ml.). This integral was again evaluated using the composite Simpson's rule as described earlier. The interval from 0 to $a$ was divided into 20 parts (i.e., $\Delta b = a/20$). The values of $\phi_a$ as a function of the radius of the cylinder $a$, are plotted in Figure 30. Since most of the energy is lost at short distances, the rise in the fraction absorbed is steep at small distances and then it levels off to reach $\phi_a = 1.0$ at infinite cylinder diameter.

A computer program to calculate (i) the area of spherical shell of radius $R$ contained inside a cylinder of radius $a$, the center of a sphere located inside the cylinder at a distance $b$ from the axis (equation 41), (ii) the dose rate at the point $b$ from a source located at a distance $R$ (equation 14), (iii) the total dose received by the point $b$ inside a cylinder of radius $a$ (equation 43), (iv) the dose received at the axis of the cylinder and (v) the fraction of total dose intercepted by the cylinder (equation 45); is presented in Appendix E along with a sample output.
Figure 30. Fraction of total emitted dose absorbed by the cylinder as a function of the radius of the cylinder.
For the purpose of mathematical manipulations, it was necessary to transform the calculated \( \phi_a \) vs. \( a \) values to a mathematical expression. The \( \phi_a \) vs. \( a \) curve was linearized by approximating it in two parts by two hyperbolae

\[
\phi_a = \frac{a}{0.215 + 0.706a} \quad a \leq 0.3 \text{ cm.}^2/\text{gm.} \quad (46)
\]

\[
\phi_a = \frac{a}{0.120 + a} \quad 0.3 < a \leq 2.6 \text{ cm.}^2/\text{gm.} \quad (47)
\]

The correlation coefficients for these two expressions were 0.9870 and 0.9999 respectively. The linearized plots are also shown in Figures (31) and (32). Thus we now have an approximate value of the integral formed after substituting equations (14) and (43) into equation (45) and subject to the limits depending upon the relative magnitudes of \( a \), \( b \) and \( R \).

C3. Prediction of the Relative Viscosity of the Fluid as a Function of the Radius of Cylinder and Comparison with Experimental Observation

The relative viscosities of the solutions contained inside different diameter capillaries filled with the radioactive saline solution can now be predicted with the help of equations (20), (34), (40) and (46) or (47). This same set of equations can be used to predict the time required for the monomer solutions in a given diameter capillary to reach a certain viscosity. A graph of the
Figure 31. Linearization of $\Phi_n$ vs. a curve, $a=0.3$ cm.
Figure 32. Linearization of $\phi_a$ vs. a curve $0.3 < a < 2.6$ cm.
predicted relative viscosities of solutions with polymerizing monomer in the capillaries of the same diameters as used in the experiments is shown in Figure 33 as a function of the total apparent dose absorbed (or total radiant energy emitted). For comparison purposes the experimentally observed relative viscosities are also plotted in the same figure. It can be seen that excellent agreement is obtained between the predicted and observed values in the initial period where polymerization of the monomer was predominant.

At present no satisfactory theoretical or experimental expression exists to account for the rate and extent of depolymerization other than a random chain scission model (Simha, [189]; Coyne, [190]). The depolymerization observed in the experiments with both $^{60}$Co and $^{32}$P at high temperature was complicated by the fact that time, temperature, radiation and oxygen all were contributing to the degradation of the polymer. No attempt was, therefore, made to predict the decreasing viscosity part of the response.
Figure 33. Predicted relative viscosities of solutions in different diameter capillaries vs. total apparent dose at 81.5°C.
Figures 34-37 depict what happens to solutions of polyacrylamide when irradiated under different conditions. All irradiations were carried out at room temperature. It is seen that above a certain critical value of polymer concentration (~0.6 g./100 ml. of solution), continued irradiation led to the crosslinking of the solution, and that the higher the concentration, the lower was the dose needed to achieve this crosslinking. These observations are in accord with those reported by Alexander and Charlesby [161] and Berkowitch [191], although the total dose needed for crosslinking as reported in this work (e.g., ~2x10^5 rads for 1% polymer) are much lower than those by Alexander and Charlesby [161] (e.g., ~1.27x10^6 rads for 1% polymer). The discrepancy could be attributed to the possibility of a lower molecular weight sample used by Alexander. Both of the above mentioned articles did not mention the phenomenon of tremendous decrease in solution viscosity in the pre-gelation period in relation to polyacrylamide (as depicted in Figures 35-37), but they did notice a slight decrease in viscosities of solutions of poly(vinylpyrrolidone) prior to gelation (also Charlesby and Alexander, [195]). As observed also in this work, the initial rate of viscosity drop was higher, higher the initial viscosity of the solution.
Figure 34. Viscosity vs. shear time response of 1% polyacrylamide solution after different amounts of irradiation at 28°C under $^{60}$Co.

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Figure 35. Viscosity vs. dose response of 0.2, 0.4, 0.6 and 1.0% solutions of polyacrylamide irradiated with 60Co at 28°C.
Figure 36. Viscosity vs. dose response of 0.1, 0.5 and 1.0% solutions of polyacrylamide in 10% salt water irradiated with $^{60}$Co at 28°C.
Figure 37. Viscosity vs. dose response of 1.5% solutions of three different polyacrylamides in 10% salt water irradiated with $^{60}$Co at 28°C.
As indicated earlier, the solutions containing less than the critical concentration of the polymer, degraded continually under irradiation, until their viscosities were close to that of water. It was frequently observed that these solutions turned opalescent during irradiation. It is quite possible that this opalescence was caused by microgels which formed during irradiation. Because of low concentration, these microgels could not link with each other and occupy the total volume and because of the fineness of their size, they remained suspended. Thus it could be argued that crosslinking occurs also in dilute solutions of polymers (of crosslinking type).

The presence of salt not only decreased the viscosity of the solution for a given dose absorbed (Figure 34), it also delayed crosslinking (Figure 36). This observation is consistent with the earlier proposal that the presence of salt decreases the hydrodynamic volume of the polymer. Under such conditions less area is available for crosslinking and consequently gelation is delayed (or may even require higher concentration). The qualitative nature of the viscosity response remains the same.

Figure 37 presents an interesting aspect of the process of radiation crosslinking of solutions of polyacrylamide prepared in three different ways. The samples RP and RX were 1.5% solutions of polyacrylamide which were obtained from irradiating 3% acrylamide solutions in 10%
salt water. Sample RX was lightly crosslinked (i.e., beyond the viscosity plateau of Figure 9), while the sample RP was not at all crosslinked (i.e., just reaching the viscosity plateau). The polymers were precipitated in methanol, washed in methanol:water (95:5) mixture, dried in vacuum oven and then appropriate quantities of the amorphous polymer dissolved in 10% saline water to prepare a 1.5% polymer solution. The sample CP was commercially available polyacrylamide. The much higher initial viscosity of the commercial sample is due to the fact that it was prepared from an acrylamide solution of much higher concentration than 3% and hence contained much higher molecular weight polymer. The purpose of this experiment was to see if a lightly crosslinked sample would need less total dose to completely crosslink. As evident from Figure 37, it took the largest total dose. It appears therefore that the amount of dose needed to complete crosslinking is a function of the hydrodynamic volume of the species in solution. Since the sample RX was prepared from lightly crosslinked polymer, its hydrodynamic volume was reduced much more than the sample RP when a non-solvent, methanol, was added to their solutions. Following the same logic, the commercial polyacrylamide solution, by virtue of its high DP, and hence a large hydrodynamic volume, crosslinked the fastest.
The phenomenon of decreasing solution viscosities in the pre-gelation region can be seen under the light of two existing theories. The first one contends that under continued irradiation more and more branched polymers are formed.

\[
\begin{align*}
\text{---} & + \quad \text{---.} + \quad \text{---} \\
\text{---.} & \quad \rightarrow \quad \text{---}
\end{align*}
\]

Since branched polymers have lower solution viscosities than the linear polymers for a given molecular weight (Morawetz, [192]), it is expected that the viscosities will drop as irradiation continues.

The second argument derives from the more recently postulated theory of macromolecular domains. In contrast with the normally assumed gaussian distribution of the density of chain segments of a macromolecule around its center of mass, the macromolecular domain model postulates an almost constant segmental density over the space occupied by a macromolecule. Under such conditions, it is easy to see that intramolecular crosslinks will be preferentially formed in the beginning of the crosslinking process. The consequent reduction in the hydrodynamic volume of the polymer would lower its solution viscosity. If the polymer is present in sufficient concentration, subsequent intermolecular linking would set the solution to a gel.
Both of the above theories do provide rationale for the experimental results qualitatively, but neither can account for such phenomenal drops in viscosities as from 300 cps. to 7 cps. for a 1% polyacrylamide solution. The present author is of the opinion that regardless of the actual crosslinking mechanism, the measured solution viscosities are that of the supernatant fluid around the gel under construction. As more crosslinks are formed more of the polymer in the fluid is accrued to the gel. This could explain why fluids of nearly water-like viscosities are obtained in all the cases (regardless of the polymer concentration and the initial viscosity). This would also explain why the recognition of gel-formation is abrupt in all cases. The previously mentioned two theories predict a gradual increase in viscosity until gel formation occurs.
E. Irradiation of Acrylamide Solution in a Typical Reservoir Fluid

In an attempt to evaluate whether the basic experimental results obtained in this work had any practical application in tertiary oil recovery, several solutions of acrylamide were irradiated at room temperature. These solutions contained salts that may be expected to occur in a typical oil reservoir. These were the following:

1. 1.5% acrylamide in 10% NaCl
2. 1.5% acrylamide in 10% CaCl₂
3. 1.5% acrylamide with 2x10⁻⁵ mole formaldehyde/mole acrylamide
4. 1.5% acrylamide in (15% NaCl + 10% CaCl₂ + 0.01% CaSO₄ + 0.01% FeSO₄)

Formaldehyde was added to solution (3) to see if it would expedite crosslinking, once the macromolecules are formed. Solution (4) contained additives such that its ionic composition was:

- Na⁺ 59,000 ppm.
- Cl⁻ 177,000 ppm.
- Ca²⁺ 36,000 ppm.
- SO₄⁻⁻ 100 ppm.

which was typical of Michigan water flood sample [173]. The relative viscosities of the solutions as a function of total dose absorbed is presented in Table A-18. The
presence of formaldehyde affected the solution viscosity adversely. Presumably irradiation fragmented the formaldehyde molecules and these fragments (e.g., ·O, ·OH, etc.) attacked the oligomers generating non-reactive species. The presence of CaCl₂ had a favorable albeit imperceptible influence on the viscosity of the solution. The solution representing a typical reservoir fluid crosslinked remarkably fast. Figure 38 compares the viscosity response of solutions (1) and (4). Whereas more than $6.5 \times 10^5$ rads were needed to crosslink 1.5% acrylamide in 10% salt (Figure 6), less than $4.2 \times 10^5$ rads crosslinked the typical reservoir fluid. In addition to the higher free radical density due to the presence of heavier ions, it is suspected that the chelating properties of Ca²⁺ and Fe²⁺ were also partially responsible for the premature gelation.
Figure 38. Relative viscosity of 1.5% acrylamide solutions in 10% salt water and in typical reservoir water irradiated with $^{60}$Co at 28°C.
CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

A few words concerning the feasibility of the application of the radiation-induced selective-reaction-rates concept to real situation are in order now. Thus far, no consideration has been given to the measures needed to ensure safe handling, storage and usage of the radioactive material. Although radioactive materials have been used before in EOR field applications; e.g., in controlling bacterial growth in the well bore (Means, [193]), injection of radioactive tracers for routine analysis etc., none of these involve the enormous quantities of dissolved radioactivity suggested in this work. It is possible to overcome some of the safety and financial problems by using pure or mixed radioactive materials of short half lives obtained from radioactive wastes -- the separation and handling costs would still be prohibitive. At the present time, since such materials are under heavy federal regulations, it was not possible to obtain any cost figures. (The cost of the 99.9% pure $^{32}\text{P}$ isotope used in the experiments was $3.00$ millicurie, or $3.00$ per ml. of the solution!) No data
could be obtained on the typical amount of flood water needed to plug the faulty formation and the benefits accrued from it in terms of increased oil production. An economic analysis was therefore not possible. However, with the information at hand, it can be safely said that any direct application of the proposed concept in EOR in the near future is not foreseeable. In the light of the observations that crosslinked gel did not form at high temperature under irradiation and that polymer solutions initially tend to lose viscosity, much experimental and safety studies must be done before the potential danger of the radioactive flood water accidentally mixing with potable water can be avoided.

The concept of size dependence of efficiency of energy transfer, however, does have promises in store -- ranging from dosage calculations from radioactive tracers dissolved in blood stream to controlling the pore size distribution in materials of industrial and academic importance. In the present work some interesting phenomena have been observed in radiation induced solution polymerization of acrylamide to high conversions and the influence of salt and temperature on the process of polymerization which should be looked into. A few conclusions and suggestions for further work are presented next.
A. Conclusions

1. The rate of radiation-induced polymerization is, as predicted, dependent upon the diameter of the capillary, being higher in larger diameter pores than in smaller diameter pores containing monomer solution subjected to the same radioactivity per unit volume.

2. The minimum concentration of acrylamide needed to produce a crosslinked polyacrylamide gel is between 1.5 - 2.0% w/v. This is in contrast with the reported values of 2.8% (Katayama et al., [176]) using chemical crosslinking agents.

3. The presence of salt increases the rate of reaction and possibly increases the molecular weight of the polymer formed. As a result, solution viscosities increase with increasing salt concentrations. This is in contrast with persulfate initiated polymerization where solution viscosities are drastically reduced with increasing amounts of salt.

4. The rate of shrinkage (per unit dose) of a gel with lower initial concentration of monomer is faster than that of a gel with higher initial monomer concentration.

5. The polymer molecular weight is severely curtailed at high temperature in the presence of radiation.

6. The presence of salt has no discernible effect on the activation energy of radiation induced polymerization.
7. Presence of salt in aqueous solutions of polyacrylamide (above the critical concentration) delays the onset of crosslinking.

8. The solution viscosity-vs.-dose data for irradiation of solutions of polyacrylamide conform to the qualitative predictions of the recently proposed theory of macromolecular domains (Aharoni [119-122]).

9. The formation of crosslinked gel starting from aqueous solution of acrylamide undergoes three distinct stages. These may be identified as (1) polymerization, (2) branching and intramolecular crosslinking and (3) intermolecular crosslinking.

10. Kinetic data for reactions in viscous media may be linearized on ln(1-x) vs. ln t coordinate axes (x = extent of conversion; t = time of reaction).

B. Suggestions for Further Work

1. A more direct and quantitative estimate of the increase of the free radical concentration in aqueous solution in the presence of salt can be obtained by irradiating solutions containing various amounts of salt and a free radical scavenger e.g., diphenylpicrylhydrazyl and determining the rate of disappearance of the latter.

2. A $^{13}$C NMR analysis would reveal whether branching occurs at the $\alpha$ position (which would then become a quaternary carbon), or $\beta$ position (resulting in a tertiary
carbon), or at the amide site (no change in carbon spectrum).

3. Degradation of a polymer under irradiation can be assumed to proceed through random chain scission. Experimental determination of molecular weights of the polymer can be made as a function of dose to define a rate constant characterizing the process of depolymerization. This could then be compared with the theoretical predictions [189, 190].

4. The monomer solution under irradiation cross-linked at 28°C but did not gel at 81°C. It stands to reason that there is a critical temperature in between where crosslinking is incipient. Study of kinetic and solution properties under such condition should provide valuable insight into the effect of radiation on polymer solutions.

5. The monomer/polymer solutions used in the experiments were not methodically deoxygenated, since the purpose was to simulate the reservoir conditions. It is felt that the results reported in this work should be compared with those obtained with rigorously deoxygenated solutions (especially the high temperature reactions).

6. Substantial reduction in the cost of radioactive material can be achieved by choosing a suitable carrier for the radioactive element, such that -- once inside the reservoir -- it undergoes ion-exchange with the ions on
the reservoir rock-surface (usually Ca$^{++}$, Mg$^{++}$, etc.) and immobilizes the radiation source. The monomer solution can be polymerized as it passes by these rocks for as long as the radioactivity lasts.

7. Direct determination of the molecular weights (e.g., through GPC or light scattering) of the polymers formed at the viscosity plateau should be made to determine the constant and $a$ in the expression formulating the onset of entanglement:

$$N_c = \text{const.} C^a$$

8. It is also recommended to investigate the extent of validity (initial monomer concentration, viscosity of the medium, type of initiation, upper and lower limits on conversion etc.) of the proposed empirical expression for reactions in viscous media by applying it to the data available in literature.

9. The expression for the fractional energy absorbed $\phi_a$ (equation 45) should be generalized to also include other radioisotopes in various media. The generalized expression would have applications in radiation therapy.
REFERENCES


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35. G. P. Willhite and J. G. Dominguez. in Ref. 173.


139. J. Sebban and E. Migirdicyan. Quoted in Ref. 131.


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TABLE A-1

RADIATION POLYMERIZATION OF 1% AQ. SOLUTIONS OF ACRYLAMIDE AT 28°C

Average dose rate 372 rads/min. (actually variable)

<table>
<thead>
<tr>
<th>t</th>
<th>Dose (rads x 10^{-4})</th>
<th>x</th>
<th>η_{rel}</th>
<th>ln(t/min.)</th>
<th>-ln(1-x)</th>
</tr>
</thead>
<tbody>
<tr>
<td>124</td>
<td>4.62</td>
<td>0.175</td>
<td>1.2</td>
<td>4.82</td>
<td>0.19</td>
</tr>
<tr>
<td>248</td>
<td>9.24</td>
<td>0.558</td>
<td>1.6</td>
<td>5.51</td>
<td>0.82</td>
</tr>
<tr>
<td>323</td>
<td>12.01</td>
<td>0.658</td>
<td>1.7</td>
<td>5.78</td>
<td>1.07</td>
</tr>
<tr>
<td>546</td>
<td>20.30</td>
<td>0.776</td>
<td>1.7</td>
<td>6.33</td>
<td>1.50</td>
</tr>
<tr>
<td>797</td>
<td>29.65</td>
<td>0.925</td>
<td>1.8</td>
<td>6.68</td>
<td>2.59</td>
</tr>
<tr>
<td>1092</td>
<td>40.61</td>
<td>1.008</td>
<td>1.9</td>
<td>7.00</td>
<td>--</td>
</tr>
<tr>
<td>1861</td>
<td>69.22</td>
<td>1.007</td>
<td>2.0</td>
<td>7.53</td>
<td>--</td>
</tr>
</tbody>
</table>

-ln(1-x) = 0.884 ln t - 4.06

correlation coefficient 0.999
### Table A-2

**Relative Viscosities of Radiation Polymerized 1% and 1.5% Aq. Solutions of Acrylamide with 5 and 10% Salt at 28°C**

Average dose rate 400 rads/min.

<table>
<thead>
<tr>
<th>Dose $10^{-4}$ rads</th>
<th>t min.</th>
<th>1% acrylamide</th>
<th>1.5% acrylamide</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>4.88</td>
<td>122</td>
<td>1.9</td>
<td>2.3</td>
</tr>
<tr>
<td>12.08</td>
<td>302</td>
<td>2.3</td>
<td>2.4</td>
</tr>
<tr>
<td>28.80</td>
<td>720</td>
<td>2.2</td>
<td>2.2</td>
</tr>
<tr>
<td>48.40</td>
<td>1210</td>
<td>2.0</td>
<td>2.2</td>
</tr>
<tr>
<td>60.00</td>
<td>1500</td>
<td>2.0</td>
<td>2.2</td>
</tr>
<tr>
<td>67.20</td>
<td>1680</td>
<td>2.0</td>
<td>2.2</td>
</tr>
<tr>
<td>72.00</td>
<td>1800</td>
<td>1.8</td>
<td>2.2</td>
</tr>
<tr>
<td>76.80</td>
<td>1920</td>
<td>6.4</td>
<td>12.1</td>
</tr>
</tbody>
</table>

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TABLE A-3

RADIATION POLYMERIZATION OF 2% AQUEOUS SOLUTIONS OF ACRYLAMIDE AT 28°C

Average dose rate 372 rads/min. (actually variable)

<table>
<thead>
<tr>
<th>t min.</th>
<th>Dose ($\text{rads} \times 10^{-4}$)</th>
<th>$x$</th>
<th>$n_{\text{rel}}$</th>
<th>$\ln(t/\text{min.})$</th>
<th>$-\ln(1-x)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>114</td>
<td>4.24</td>
<td>0.241</td>
<td>2.08</td>
<td>4.74</td>
<td>0.28</td>
</tr>
<tr>
<td>228</td>
<td>8.47</td>
<td>0.619</td>
<td>5.44</td>
<td>5.43</td>
<td>0.97</td>
</tr>
<tr>
<td>319</td>
<td>11.87</td>
<td>0.794</td>
<td>7.97</td>
<td>5.77</td>
<td>1.58</td>
</tr>
<tr>
<td>604</td>
<td>22.46</td>
<td>0.818</td>
<td>6.45</td>
<td>6.40</td>
<td>1.70</td>
</tr>
<tr>
<td>744</td>
<td>27.69</td>
<td>0.873</td>
<td>7.36</td>
<td>6.61</td>
<td>2.06</td>
</tr>
<tr>
<td>1208</td>
<td>44.93</td>
<td>1.024</td>
<td>29.82</td>
<td>7.10</td>
<td>--</td>
</tr>
<tr>
<td>1903</td>
<td>70.80</td>
<td>--</td>
<td>GEL</td>
<td>7.55</td>
<td>--</td>
</tr>
</tbody>
</table>

$-\ln(1-x) = 0.906 \ln t - 4.0$

correlation coefficient 0.986

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TABLE A-4

RADIATION POLYMERIZATION OF 3% AQ. SOLUTION
OF ACRYLAMIDE AT 28°C

Average dose rate 372 rads/min. Actually 394 rads/min.

<table>
<thead>
<tr>
<th>t min.</th>
<th>Dose rads $\times 10^{-4}$</th>
<th>x</th>
<th>$n_{rel}$</th>
<th>ln(t/min.)</th>
<th>$-\ln(1-x)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>63</td>
<td>2.36</td>
<td>-0.023</td>
<td>1.0</td>
<td>4.14</td>
<td>0.0</td>
</tr>
<tr>
<td>127</td>
<td>4.73</td>
<td>0.404</td>
<td>18.7</td>
<td>4.84</td>
<td>0.518</td>
</tr>
<tr>
<td>191</td>
<td>7.09</td>
<td>0.495</td>
<td>26.4</td>
<td>5.25</td>
<td>0.683</td>
</tr>
<tr>
<td>318</td>
<td>11.82</td>
<td>0.633</td>
<td>36.5</td>
<td>5.76</td>
<td>1.002</td>
</tr>
<tr>
<td>445</td>
<td>16.55</td>
<td>0.678</td>
<td>38.2</td>
<td>6.10</td>
<td>1.133</td>
</tr>
<tr>
<td>572</td>
<td>21.28</td>
<td>0.764</td>
<td>56.9</td>
<td>6.35</td>
<td>1.444</td>
</tr>
<tr>
<td>699</td>
<td>26.00</td>
<td>0.800</td>
<td>143.3</td>
<td>6.55</td>
<td>1.609</td>
</tr>
<tr>
<td>744</td>
<td>27.69</td>
<td>0.776</td>
<td>948.6</td>
<td>6.61</td>
<td>1.496</td>
</tr>
</tbody>
</table>

$-\ln(1-x) = 0.62 \ln t - 2.57$

correlation coefficient 0.986
TABLE A-5

RADIATION POLYMERIZATION OF AQ. SOLUTIONS
OF 3% ACRYLAMIDE WITH 5% SALT AT 28°C

Average dose rate 372 rads/min. Actually 350 rads/min.

<table>
<thead>
<tr>
<th>t (min.)</th>
<th>Dose rads x 10^{-4}</th>
<th>x</th>
<th>n_{rel}</th>
<th>ln(t/min.)</th>
<th>-ln(1-x)</th>
</tr>
</thead>
<tbody>
<tr>
<td>56</td>
<td>2.10</td>
<td>0.001</td>
<td>1.0</td>
<td>4.03</td>
<td>0.001</td>
</tr>
<tr>
<td>113</td>
<td>4.20</td>
<td>0.642</td>
<td>39.3</td>
<td>4.73</td>
<td>1.027</td>
</tr>
<tr>
<td>169</td>
<td>6.30</td>
<td>0.733</td>
<td>54.4</td>
<td>5.13</td>
<td>1.321</td>
</tr>
<tr>
<td>282</td>
<td>10.50</td>
<td>0.825</td>
<td>66.2</td>
<td>5.64</td>
<td>1.743</td>
</tr>
<tr>
<td>395</td>
<td>14.70</td>
<td>0.904</td>
<td>84.7</td>
<td>5.98</td>
<td>2.343</td>
</tr>
<tr>
<td>508</td>
<td>18.90</td>
<td>0.935</td>
<td>127.8</td>
<td>6.23</td>
<td>2.733</td>
</tr>
<tr>
<td>621</td>
<td>23.10</td>
<td>0.975</td>
<td>1622.2</td>
<td>6.43</td>
<td>3.689</td>
</tr>
<tr>
<td>734</td>
<td>27.30</td>
<td>0.900</td>
<td>GEL</td>
<td>6.60</td>
<td>2.303</td>
</tr>
</tbody>
</table>

-ln(1-x) = 1.17 \ln t - 4.6

correlation coefficient 0.984
TABLE A-6

RADIATION POLYMERIZATION OF AQ. SOLUTIONS
OF 3% ACRYLAMIDE AND 10% SALT AT 28°C

Average dose rate 372 rads/min. Actually 355 rads/min.

<table>
<thead>
<tr>
<th>t min.</th>
<th>Dose rads x 10^-4</th>
<th>x</th>
<th>η_{rel}</th>
<th>ln(t/min.)</th>
<th>-ln(1-x)</th>
</tr>
</thead>
<tbody>
<tr>
<td>57</td>
<td>2.13</td>
<td>0.379</td>
<td>16.8</td>
<td>4.04</td>
<td>0.48</td>
</tr>
<tr>
<td>115</td>
<td>4.26</td>
<td>0.794</td>
<td>54.0</td>
<td>4.75</td>
<td>1.58</td>
</tr>
<tr>
<td>172</td>
<td>6.39</td>
<td>0.855</td>
<td>63.1</td>
<td>5.15</td>
<td>1.93</td>
</tr>
<tr>
<td>286</td>
<td>10.65</td>
<td>0.941</td>
<td>65.5</td>
<td>5.66</td>
<td>2.83</td>
</tr>
<tr>
<td>401</td>
<td>14.91</td>
<td>0.941</td>
<td>67.1</td>
<td>5.99</td>
<td>2.83</td>
</tr>
<tr>
<td>530</td>
<td>19.71</td>
<td>0.953</td>
<td>96.6</td>
<td>6.27</td>
<td>3.06</td>
</tr>
<tr>
<td>630</td>
<td>23.43</td>
<td>0.941</td>
<td>209.5</td>
<td>6.45</td>
<td>2.83</td>
</tr>
<tr>
<td>826</td>
<td>30.73</td>
<td>--</td>
<td>GEL</td>
<td>6.72</td>
<td>--</td>
</tr>
</tbody>
</table>

-ln(1-x) = 1.17 ln t - 4.09

correlation coefficient 0.964
TABLE A-7

RADIATION POLYMERIZATION OF AQ. SOLUTIONS
OF 3% ACRYLAMIDE WITH NO SALT AT 80°C

Average dose rate 372 rads/min. Actually 394 rads/min.

<table>
<thead>
<tr>
<th>t min.</th>
<th>Dose rads x 10^{-4}</th>
<th>x</th>
<th>n_{rej}</th>
<th>ln(t/min.)</th>
<th>-ln(1-x)</th>
</tr>
</thead>
<tbody>
<tr>
<td>63</td>
<td>2.36</td>
<td>0.672</td>
<td>18.7</td>
<td>4.14</td>
<td>1.12</td>
</tr>
<tr>
<td>133</td>
<td>4.93</td>
<td>0.922</td>
<td>31.1</td>
<td>4.89</td>
<td>2.55</td>
</tr>
<tr>
<td>191</td>
<td>7.09</td>
<td>0.861</td>
<td>31.3</td>
<td>5.25</td>
<td>1.97</td>
</tr>
<tr>
<td>381</td>
<td>11.82</td>
<td>0.910</td>
<td>22.3</td>
<td>5.76</td>
<td>2.41</td>
</tr>
<tr>
<td>445</td>
<td>16.55</td>
<td>0.919</td>
<td>15.3</td>
<td>6.10</td>
<td>2.51</td>
</tr>
<tr>
<td>572</td>
<td>21.28</td>
<td>0.919</td>
<td>15.0</td>
<td>6.35</td>
<td>2.51</td>
</tr>
<tr>
<td>826</td>
<td>30.73</td>
<td>0.932</td>
<td>11.2</td>
<td>6.72</td>
<td>2.69</td>
</tr>
<tr>
<td>1525</td>
<td>56.74</td>
<td>0.858</td>
<td>7.1</td>
<td>7.33</td>
<td>1.95</td>
</tr>
</tbody>
</table>

-ln(1-x) = 0.62 \ln t - 1.34

correlation coefficient 0.955
TABLE A-8

RADIATION POLYMERIZATION OF AQ. SOLUTIONS
OF ACRYLAMIDE 3% WITH 5% SALT AT 80°C

Average dose rate 372 rads/min. Actually 350 rads/min.

<table>
<thead>
<tr>
<th>t min.</th>
<th>Dose rads x 10^-4</th>
<th>x</th>
<th>n_{rel}</th>
<th>ln(t/min.)</th>
<th>-ln(1-x)</th>
</tr>
</thead>
<tbody>
<tr>
<td>56</td>
<td>2.10</td>
<td>0.691</td>
<td>17.3</td>
<td>4.03</td>
<td>1.17</td>
</tr>
<tr>
<td>118</td>
<td>4.38</td>
<td>0.898</td>
<td>25.6</td>
<td>4.77</td>
<td>2.28</td>
</tr>
<tr>
<td>169</td>
<td>6.30</td>
<td>0.944</td>
<td>30.2</td>
<td>5.13</td>
<td>2.88</td>
</tr>
<tr>
<td>282</td>
<td>10.50</td>
<td>0.965</td>
<td>22.7</td>
<td>5.64</td>
<td>3.35</td>
</tr>
<tr>
<td>395</td>
<td>14.70</td>
<td>0.971</td>
<td>14.7</td>
<td>5.98</td>
<td>3.54</td>
</tr>
<tr>
<td>508</td>
<td>18.90</td>
<td>0.990</td>
<td>15.5</td>
<td>6.23</td>
<td>4.61</td>
</tr>
<tr>
<td>734</td>
<td>27.30</td>
<td>0.986</td>
<td>10.7</td>
<td>6.60</td>
<td>4.27</td>
</tr>
<tr>
<td>1355</td>
<td>50.40</td>
<td>0.990</td>
<td>8.6</td>
<td>7.21</td>
<td>4.61</td>
</tr>
</tbody>
</table>

-ln(1-x) = 1.27 \ln t - 3.82

correlation coefficient 0.946
TABLE A-9

RADIATION POLYMERIZATION OF AQ. SOLUTIONS
OF 3% ACRYLAMIDE WITH 10% SALT AT 80°C

Average dose rate 372 rads/min. Actually 355 rads/min.

<table>
<thead>
<tr>
<th>t min.</th>
<th>Dose rads x 10^-4</th>
<th>x</th>
<th>η rel</th>
<th>ln(t/min.)</th>
<th>-ln(1-x)</th>
</tr>
</thead>
<tbody>
<tr>
<td>57</td>
<td>2.13</td>
<td>0.781</td>
<td>21.1</td>
<td>4.04</td>
<td>1.52</td>
</tr>
<tr>
<td>119</td>
<td>4.44</td>
<td>0.925</td>
<td>27.5</td>
<td>4.78</td>
<td>2.59</td>
</tr>
<tr>
<td>172</td>
<td>6.39</td>
<td>0.942</td>
<td>28.1</td>
<td>5.15</td>
<td>2.87</td>
</tr>
<tr>
<td>286</td>
<td>10.65</td>
<td>0.985</td>
<td>23.4</td>
<td>5.66</td>
<td>4.20</td>
</tr>
<tr>
<td>401</td>
<td>14.91</td>
<td>0.991</td>
<td>17.7</td>
<td>5.99</td>
<td>4.71</td>
</tr>
<tr>
<td>515</td>
<td>19.17</td>
<td>0.997</td>
<td>16.2</td>
<td>6.24</td>
<td>5.81</td>
</tr>
<tr>
<td>744</td>
<td>27.69</td>
<td>0.991</td>
<td>8.8</td>
<td>6.61</td>
<td>4.71</td>
</tr>
<tr>
<td>1374</td>
<td>51.12</td>
<td>0.997</td>
<td>9.1</td>
<td>7.23</td>
<td>5.81</td>
</tr>
</tbody>
</table>

-ln(1-x) = 1.66 ln t - 5.33

correlation coefficient 0.974

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# TABLE A-10

**APPROXIMATE DOSE NEEDED FOR CROSSLINKING OF AQUEOUS SOLUTIONS OF ACRYLAMIDE AT ROOM TEMPERATURE**

<table>
<thead>
<tr>
<th>% AAm</th>
<th>Rads x $10^{-4}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>100.8</td>
</tr>
<tr>
<td>2.0</td>
<td>57.6</td>
</tr>
<tr>
<td>2.5</td>
<td>43.2</td>
</tr>
<tr>
<td>3.0</td>
<td>25.7</td>
</tr>
<tr>
<td>4.0</td>
<td>12.0</td>
</tr>
<tr>
<td>5.0</td>
<td>3.6</td>
</tr>
</tbody>
</table>
TABLE A-11

VOLUME OF EXPELLED WATER (% OF TOTAL VOLUME)
AS A FUNCTION OF TOTAL DOSE ABSORBED
BY 2% AND 5% ACRYLAMIDE SOLUTIONS

<table>
<thead>
<tr>
<th></th>
<th>2% AAm</th>
<th></th>
<th>5% AAm</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>D x 10^-4 rads</strong></td>
<td><strong>% of total volume</strong></td>
<td><strong>D x 10^-4 rads</strong></td>
<td><strong>% of total volume</strong></td>
</tr>
<tr>
<td>1.0</td>
<td>0.0</td>
<td>0.22</td>
<td>0.0</td>
</tr>
<tr>
<td>1.68</td>
<td>6.9</td>
<td>0.92</td>
<td>5.3</td>
</tr>
<tr>
<td>2.56</td>
<td>7.4</td>
<td>1.80</td>
<td>6.6</td>
</tr>
<tr>
<td>2.80</td>
<td>7.9</td>
<td>2.04</td>
<td>6.8</td>
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<tr>
<td>3.62</td>
<td>13.0</td>
<td>2.86</td>
<td>9.5</td>
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<td>4.34</td>
<td>16.3</td>
<td>3.38</td>
<td>10.8</td>
</tr>
<tr>
<td>4.86</td>
<td>20.7</td>
<td>4.10</td>
<td>11.6</td>
</tr>
<tr>
<td>5.74</td>
<td>32.7</td>
<td>4.98</td>
<td>12.9</td>
</tr>
</tbody>
</table>

Original sample compositions:

2%: 392 g. H₂O + 8 g. acrylamide
5%: 380 g. H₂O + 20 g. acrylamide

Dose rate:

400 rads/min.
TABLE A-12

RADIATION POLYMERIZATION OF AQ. SOLUTIONS OF 3% ACRYLAMIDE AND 10% SALT WITH 1mCi/ml. OF $^{32}$P DISSOLVED IN IT

Dose rate: $I = 21.88e^{-3.385 \times 10^{-5} t}$ rads/min.

Total Dose: $D = 6.46 \times 10^{5}(1-e^{-3.385 \times 10^{-5}t})$ rad.

Relative Viscosities of the Solutions:

<table>
<thead>
<tr>
<th>$t$ hrs.</th>
<th>$D$ rads $\times 10^{-4}$</th>
<th>Diameter of the capillary (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0.381</td>
</tr>
<tr>
<td>12.8</td>
<td>1.67</td>
<td></td>
</tr>
<tr>
<td>28.8</td>
<td>3.70</td>
<td></td>
</tr>
<tr>
<td>69</td>
<td>8.51</td>
<td></td>
</tr>
<tr>
<td>127.5</td>
<td>14.9</td>
<td></td>
</tr>
<tr>
<td>160</td>
<td>18.1</td>
<td></td>
</tr>
<tr>
<td>167.3</td>
<td>18.8</td>
<td></td>
</tr>
<tr>
<td>225.8</td>
<td>23.9</td>
<td></td>
</tr>
<tr>
<td>318.5</td>
<td>31.3</td>
<td></td>
</tr>
<tr>
<td>467</td>
<td>41.1</td>
<td></td>
</tr>
<tr>
<td>703.8</td>
<td>51.6</td>
<td></td>
</tr>
<tr>
<td>1195</td>
<td>59.4</td>
<td></td>
</tr>
</tbody>
</table>

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**TABLE A-13**

RELATIVE VISCOSITY VS. REACTION TIME FOR PERSULFATE INITIATED POLYMERIZATION OF ACRYLAMIDE AT 80°C

<table>
<thead>
<tr>
<th>time min.</th>
<th>1%</th>
<th>2%</th>
<th>3%</th>
</tr>
</thead>
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<tr>
<td></td>
<td>0%</td>
<td>5%</td>
<td>10%</td>
</tr>
<tr>
<td>35</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>65</td>
<td>1.5</td>
<td>1.3</td>
<td>1.3</td>
</tr>
<tr>
<td>125</td>
<td>1.5</td>
<td>1.3</td>
<td>1.2</td>
</tr>
<tr>
<td>185</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>365</td>
<td>1.3</td>
<td>1.1</td>
<td>1.0</td>
</tr>
<tr>
<td>1740</td>
<td>1.5</td>
<td>1.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>
TABLE A-14

SHEAR DEGRADATION OF IRRADIATED POLYACRYLAMIDE

Initial viscosity: 25.12 for 0% salt, 24.11 for 10% salt

Shear rate: @ 12 rpm

Relative Viscosities of the Solutions

<table>
<thead>
<tr>
<th>time under shear min:sec.</th>
<th>0.5% Polyacrylamide</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.17 x 10^4 rads</td>
</tr>
<tr>
<td>Salt Content</td>
<td>0%</td>
</tr>
<tr>
<td>0%</td>
<td>14.2</td>
</tr>
<tr>
<td>10%</td>
<td>13.8</td>
</tr>
<tr>
<td></td>
<td>13.7</td>
</tr>
<tr>
<td></td>
<td>13.7</td>
</tr>
<tr>
<td></td>
<td>13.7</td>
</tr>
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<td></td>
<td>13.7</td>
</tr>
<tr>
<td></td>
<td>13.5</td>
</tr>
<tr>
<td></td>
<td>13.5</td>
</tr>
<tr>
<td></td>
<td>13.5</td>
</tr>
<tr>
<td></td>
<td>13.4</td>
</tr>
<tr>
<td></td>
<td>13.1</td>
</tr>
</tbody>
</table>

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# TABLE A-15

**VISCOSITIES OF IRRADIATED POLYACRYLAMIDE SOLUTIONS**

<table>
<thead>
<tr>
<th>Concentration of Polyacrylamide in Water</th>
<th>0.2%</th>
<th>0.4%</th>
<th>0.6%</th>
<th>1.0%</th>
</tr>
</thead>
<tbody>
<tr>
<td>D$_4$ rads x $10^{-4}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>5.3</td>
<td>16.6</td>
<td>43.0</td>
<td>306.5</td>
</tr>
<tr>
<td>3.37</td>
<td></td>
<td></td>
<td></td>
<td>22.3</td>
</tr>
<tr>
<td>6.01</td>
<td></td>
<td></td>
<td>3.5</td>
<td></td>
</tr>
<tr>
<td>6.73</td>
<td></td>
<td></td>
<td></td>
<td>11.7</td>
</tr>
<tr>
<td>11.88</td>
<td>1.8</td>
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<td></td>
</tr>
<tr>
<td>13.46</td>
<td></td>
<td>2.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13.86</td>
<td>1.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14.15</td>
<td></td>
<td></td>
<td></td>
<td>7.3</td>
</tr>
<tr>
<td>14.83</td>
<td></td>
<td>2.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>16.03</td>
<td></td>
<td>2.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>16.17</td>
<td></td>
<td></td>
<td>10.3</td>
<td></td>
</tr>
<tr>
<td>18.86</td>
<td></td>
<td></td>
<td>38.1</td>
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</tr>
<tr>
<td>19.80</td>
<td></td>
<td></td>
<td>Gel</td>
<td></td>
</tr>
<tr>
<td>20.04</td>
<td></td>
<td></td>
<td>34.5</td>
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</tr>
<tr>
<td>21.18</td>
<td></td>
<td>1.8</td>
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</tr>
<tr>
<td>23.10</td>
<td>1.2</td>
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<td></td>
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</tr>
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<td>32.34</td>
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<td></td>
<td>Gel</td>
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<tr>
<td>35.64</td>
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<td>1.8</td>
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</tr>
<tr>
<td>41.58</td>
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<td>48.10</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>50.83</td>
<td>1.1</td>
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<tr>
<td>D rads x 10^{-4}</td>
<td>Concentration of Polyacrylamide</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-----------------</td>
<td>---------------------------------</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.1%</td>
<td>0.5%</td>
<td>1.0%</td>
<td></td>
</tr>
<tr>
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<td>2.0</td>
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<tr>
<td>4.68</td>
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<td>8.0</td>
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</tr>
<tr>
<td>9.36</td>
<td>1.3</td>
<td>2.1</td>
<td>5.5</td>
<td></td>
</tr>
<tr>
<td>18.72</td>
<td>1.2</td>
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<td>6.3</td>
<td></td>
</tr>
<tr>
<td>28.47</td>
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<td>2.1</td>
<td>77.1</td>
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</tr>
<tr>
<td>76.05</td>
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<td>3.0</td>
<td>Gel</td>
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<tr>
<td>150.93</td>
<td>1.2</td>
<td>2.7</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### TABLE A-17

**VISCOSITIES UPON IRRADIATION OF VARIOUS POLYACRYLAMIDE SOLUTIONS**

*(1.5% in 10% Salt Water)*

<table>
<thead>
<tr>
<th>Viscosities in cps</th>
<th>D rads x 10^-4</th>
<th>#1 Comm PAAM.</th>
<th>#2 RPAAM.</th>
<th>#3 RXPAAM.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
<td>397.9</td>
<td>26.1</td>
<td>23.5</td>
</tr>
<tr>
<td></td>
<td>1.17</td>
<td>170.5</td>
<td>19.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.34</td>
<td>71.5</td>
<td>17.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.93</td>
<td>43.7</td>
<td></td>
<td>16.0</td>
</tr>
<tr>
<td></td>
<td>3.51</td>
<td>Gel</td>
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<td></td>
</tr>
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<td>4.68</td>
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<td>12.2</td>
<td>15.2</td>
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<td>7.02</td>
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<td>16.2</td>
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<td>11.70</td>
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<tr>
<td></td>
<td>14.04</td>
<td></td>
<td></td>
<td>Gel</td>
</tr>
</tbody>
</table>
TABLE A-18

CROSSLINKING OF ACRYLAMIDE IN A TYPICAL RESERVOIR FLUID

Solution #1. 1.5% acrylamide 10% salt

#2. 1.5% acrylamide 10% CaCl₂

#3. 1.5% acrylamide + 2x10⁻⁵ mole Formaldehyde/mole acrylamide.

#4. 1.5% acrylamide + 15% NaCl + 10% CaCl₂ + 0.01% CaSO₄ + 0.01% FeSO₄

Relative viscosities

<table>
<thead>
<tr>
<th>D rads x 10⁻⁴</th>
<th>#1</th>
<th>#2</th>
<th>#3</th>
<th>#4</th>
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<tbody>
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<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>4.68</td>
<td>6.4</td>
<td>7.4</td>
<td>1.7</td>
<td>19.0</td>
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<tr>
<td>9.36</td>
<td>6.9</td>
<td>7.7</td>
<td>2.3</td>
<td>16.0</td>
</tr>
<tr>
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<td>2.4</td>
<td>13.7</td>
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<td>12.2</td>
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<td>1.9</td>
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<td>1.8</td>
<td>81.8</td>
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<td>1.7</td>
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<td>46.80</td>
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<td>3.5</td>
<td>1.6</td>
<td>Gel</td>
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<td>51.48</td>
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<td>3.2</td>
<td>1.6</td>
<td></td>
</tr>
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<td>56.16</td>
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<td>3.2</td>
<td></td>
<td></td>
</tr>
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<td>60.84</td>
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<td>1.4</td>
<td></td>
</tr>
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<td>70.20</td>
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<td>1.4</td>
<td></td>
</tr>
</tbody>
</table>

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APPENDIX B

Bl. Irradiation of Aqueous Solutions of Acrylonitrile with Various Additives

Radiation induced polymerization of acrylonitrile was investigated as an alternative pusher fluid -- the assumption being that suitable conditions of pH and radiation could facilitate partial hydrolysis of acrylonitrile to acrylamide.

In the presence of a strong acid or a base, a nitrile in aqueous solution reacts with water at reflux temperature to produce a carboxylic acid in the following manner:

\[
\text{CH}_2\text{=CH-C\equiv N} + 2 \text{H}_2\text{O} \xrightarrow{\text{H}^+, \text{OH}^-} \text{CH}_2\text{=CH-C-OH} + \text{NH}_3
\]

In the presence of excess NaOH, the carboxylic acid will be converted to its sodium salt. Because of strong intermolecular association solutions of poly(acrylic acid) are more viscous than a solution of poly (acrylamide) of comparable concentration. Since acrylonitrile (27¢/lb.) is almost half as expensive as acrylamide (58¢/lb.); attempts were made to create suitable
conditions to induce the transformation of aqueous solutions of acrylonitrile to viscous solutions of poly (acrylic acid) with the help of radiation. Nine solutions of 2, 3 and 4% acrylonitrile were prepared in fresh water, 0.1 N \( \text{H}_2\text{SO}_4 \) and mole/mole \( \text{NaOH} \). After an exposure of \( 2.4 \times 10^4 \) rads, it was observed that while a uniform and fine emulsion of poly acrylonitrile was formed in the neutral and acidic solutions, no such occurrence was noted in the basic solutions. Strong \( \text{NH}_3 \) evolution was noticed in this case. Apparently, radiation could not convert acrylonitrile to acrylic acid at room temperature in the presence of acid, but it did convert acrylonitrile to sodium acrylate in the presence of \( \text{NaOH} \) at room temperature. It was also noted that the yield (determined gravimetrically) of polyacrylonitrile in the acidic medium (33%) was significantly higher than that in neutral medium (16%) for the 4% solution. The difference in yield and the yield itself diminished with the monomer concentration (8% in acidic solution vs. 7% in the neutral solution at 2% monomer concentration). The polymer formed in the neutral medium could be completely degraded if heated in the presence of mole/mole \( \text{NaOH} \).

Another set of samples with 3% acrylonitrile in various media containing i) no additives, ii) 10% salt
iii) 2% HCl, iv) 10% HCl, v) 20% HCl, vi) 10% HCl with 10% salt and vii) mole/mole NaOH with 10% salt was also irradiated. Again, the sample containing NaOH was converted into a solution of sodium acrylate. From the thickness of the emulsion formed after a total dose of $4.8 \times 10^5$ rads it was inferred that the presence of salt enhanced the rate of reaction and that increasing strengths of the acid decreased the rate. All these emulsions grew thicker when heated indicating that further reaction occurred even though there was no irradiation. Such an observation proves the existence of living polymer ends in the emulsified particles.

B2. Thermally Induced Crosslinking of Acrylamide Solutions at 80°C.

Since the purpose of the present work was to produce a crosslinked gel under reservoir conditions, but continual decrease in viscosity was observed at high temperature in the presence of radiation; it was apparent that crosslinking agents must be used to counteract this undesirable phenomenon. A few experiments designed to study the crosslinking behavior of acrylamide at high temperature are discussed in the following paragraphs.

1. The polymerization and subsequent crosslinking of molten acrylamide (>80°C) is extremely rapid in the presence of 2M $\text{H}_2\text{SO}_4$. There is a short ($\approx 3-5$ minutes) induction
period. An extremely hard (not brittle) white solid is obtained. The initiation is probably through some peroxide formation in the presence of $\text{H}_2\text{SO}_4$. The extent of reaction can be controlled by cooling the system. The product in this case is clear although still insoluble in water.

Molten acrylamide in the presence of concentrated HCl did not show any reaction.

The following experiments were conducted under nitrogen in 20 ml. screw cap test tubes in a constant temperature ($80^\circ\text{C}$) bath. Sample volumes were 10 ml.

2. 10% acrylamide + few drops of 2M $\text{H}_2\text{SO}_4$: polymer formed is not of very high viscosity.

3. 10% acrylamide + few drops of 36% HCl: nothing happens.

4. 1% polyacrylamide in 1% NaCl and 1% $\text{K}_2\text{Cr}_2\text{O}_7$: (the polymer was obtained from radiation polymerization of 5% acrylamide solution): crosslinking observed after 3 days.

5. 5% solution of (radiation polymerized) polyacrylamide: retained its viscosity during the observation period (~45 days).

6. 1% polyacrylamide with 1% Al($\text{SO}_4$)$_3$ and 1% citric acid: (polymer obtained in the manner of experiment #4): viscosity of the solution increased but no crosslinking observed.

7. 0.1% commercial polyacrylamide + 1% $\text{Na}_2\text{Cr}_2\text{O}_7$ + 1% NaCl: nothing happens.
8. 1% polyacrylamide, 1% NaCl, 1% Na₂Cr₂O₇ (polymer obtained in the manner of experiment #4): crosslinking in 4 days. Thus Na₂Cr₂O₇ works as efficiently as K₂Cr₂O₇.

9. 0.5% polyacrylamide, 1% Na₂Cr₂O₇ + 1% NaCl (polymer obtained in the manner of experiment #4): crosslinking observed in 4 days.

10. 3% acrylamide + 5% salt + 1% Na₂Cr₂O₇: irradiated at 80°C up to 3.1x10⁵ rads: no polymerization observed. Apparently Cr₂O₇⁻ caused oxidative degradation of the polymer.

11. 3% acrylamide + 5% salt + 1% Na₂Cr₂O₇: irradiated at 80°C up to 6.3x10⁴ rads: (no polymerization observed): kept in the temperature bath at 80°C without radiation for 7 days. Green precipitate, and no viscosity increase observed.

12. 3% acrylamide + 5% salt: irradiated at 80°C up to 7.1x10⁴ rads. Polymer was formed. 1% Na₂Cr₂O₇ added to the solution and it was kept at 80°C. Gelation observed after 12 days. It appears from experiments 10, 11 and 12 that presence of Na₂Cr₂O₇ during irradiation is deleterious to polymerization.

13. 3% acrylamide + 1% CoCl₂ irradiated at 80°C up to 9.4x10⁴ rads: polymerization but no crosslinking.

14. 3% acrylamide + 5% salt + 1% CoCl₂ irradiated at 80°C up to 8.4x10⁴ rads. Polymerization was observed. It was then kept at 80°C without irradiation for 6 days. No decrease in viscosity nor crosslinking was observed.
15. Sample was prepared in the same manner as in experiment 14. 2.5 ml. of 0.5 N NaOH (corresponding to 30% hydrolysis of amide groups) was added to it before it was put in the temperature bath at 80°C. Increased viscosity was observed but no gelation occurred.
APPENDIX C

Electron Density Correction Factor for Different Solutions of Acrylamide Used in the Experiments

The total dose $D_S$ absorbed by the sample under consideration is related to the dose $D_F$ measured by the Fricke dosimeter in the following manner (Spinks and Wood, 1964),

$$D_S = D_F \cdot \frac{(\mu a/e)_S}{(\mu a/l)_F} = D_F \cdot \frac{(Z/A)_S}{(Z/A)_F} \text{ (in the Compton region)}$$

where $(Z/A)_S$ is the ratio of atomic number to the atomic weight of the sample and $(Z/A)_F$ is the same for the Fricke solution. This ratio for a mixture of components is defined thus:

$$(Z/A)_M = \sum_i W_i (Z/A)_i$$

where $W_i$ is the weight fraction of component $i$ in the mixture. If the component $i$ is not an element; its $(Z/A)$ can be calculated in this way:

$$(Z/A)_i = \sum_j W_j (Z/A)_j$$

where, again, $W_j$ is the weight fraction of element $j$ in the component $i$. 

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All of the above relations are true strictly for monoenergetic photons in the Compton region. This fortunately, is the case for the photons emitted from $^{60}$Co (1.25 MeV). It is understood that if the incident beam is polyenergetic, extending beyond the Compton region, the mass energy absorption coefficient ($\mu_a/e$) will vary and a mean value must be found by the method of corresponding weight fractions.

$$(Z/A)_F = (Z/A)_{0.8N\ H_2SO_4} = 0.553$$

(Spinks and Wood, 1964, p. 88)

$$\text{Acrylamide} \quad \begin{array}{c}
\text{H} \\
\text{H} \\
\text{C} = \text{C} - \text{C} \\
\text{NH}
\end{array}$$

$$(Z/A)_{\text{AAm}} = \frac{1}{71} \left( 3.12 \cdot \frac{6}{12} + 5 \cdot \frac{1}{1} + 16 \cdot \frac{8}{16} + 14 \cdot \frac{7}{14} \right) = 0.535$$

Water

$$(Z/A)_{\text{H}_2\text{O}} = \frac{1}{18} \left( 2 \cdot \frac{1}{1} + 16 \cdot \frac{8}{16} \right) = 0.556$$

Salt

$$(Z/A)_{\text{NaCl}} = \frac{1}{58.5} \left( 23 \cdot \frac{11}{23} + 35.5 \cdot \frac{17}{35.5} \right) = 0.479$$

3% solution of acrylamide (3g. AAm in 100 g. water)

$$(Z/A)_{\text{o}} = \frac{3}{103} \cdot (0.535) + \frac{100}{103} (0.556) = 0.555$$

3% acrylamide in 5% salt solution

(3g. AAm + 5g. NaCl + 100g. H$_2$O)
\[
(Z/A)_5 = \frac{100}{108} (0.556) + \frac{3}{108} (0.535) + \frac{5}{108} (0.479) \\
= 0.552
\]

3% acrylamide in 10% salt solution
(3g. AAm + 10g. NaCl + 100g. H₂O)

\[
(Z/A)_{10} = \frac{100}{113} (0.556) + \frac{3}{113} (0.535) + \frac{10}{113} (0.479) \\
= 0.549
\]

Thus the dose absorbed by different solutions are related to that measured by the Fricke dosimeter:

3% acrylamide: \( \frac{D}{D_F} = \frac{0.555}{0.553} = 1.004 \)

3% acrylamide in 5% salt solution:

\( \frac{D}{D_F} = \frac{0.552}{0.553} = 0.998 \)

3% acrylamide in 10% salt solution:

\( \frac{D}{D_F} = \frac{0.549}{0.553} = 0.993 \)

The dose absorbed by the solutions exposed to the same intensity of radiation, decreases as their salt content increases!
APPENDIX D

Calculation of Surface Area of a Spherical Shell
of Radius R Contained Inside a Cylinder
of Radius a

Reference: Figures 18, 26 and 39

Origin of the coordinate axes located at the center of the sphere.

Equation of the sphere \( z^2 = R^2 - x^2 - y^2 \) \hspace{1cm} (1)

Equation of the cylinder \( 0 = a^2 - x^2 - (y + b)^2 \) \hspace{1cm} (2)

or in cylindrical coordinates:

Equation of the sphere \( r_x^2 = R^2 - z^2 \)

Equation of the cylinder \( r_c^2 + 2r_c b \sin \theta + b^2 = a^2 \) \hspace{1cm} (4)

where \( b \) is the distance of the center of the sphere from the axis of the cylinder, and \( 0 < b < a \).

Equation (4) can be solved for \( r_c \) to give:

\[
 r_c = \frac{1}{2} \left( -2b \sin \theta \pm \sqrt{4b^2 \sin^2 \theta - 4(b^2 - a^2)} \right)
 = -b \sin \theta + \sqrt{a^2 - b^2 \cos^2 \theta}
\]

(5)

where we chose the +ve sign to ensure \( r_c > 0 \).
Figure 39. Portion of a Sphere Contained Inside a Cylinder under Different Conditions
The angle $\theta_x$, at which the sphere and the cylinder intersect in the $x$, $y$ plane is given by:

$$r_{cylinder} = r_c = r_{sphere} = R$$

and from the relationship $x = r \cos \theta$ and $y = r \sin \theta$; we obtain

$$R^2 + 2Rb \sin \theta_x + b^2 = a^2$$

or

$$\theta_x = \sin^{-1} \left( \frac{a^2 - b^2 - R^2}{2bR} \right) \quad (6)$$

Now, the projection on the $x$, $y$ plane of the area of interest to us (portion of spherical shell contained inside the cylinder) is shown hatched in Figure 39. If we consider only the portion between $-\pi/2 \leq \theta \leq \pi/2$, the actual area of concern is four times of this calculated area.

From secant theorem for area in analytical geometry, we know that the area of a surface $Z = f(x,y)$ above the $x$, $y$ plane can be calculated from its projection on the $x$, $y$ plane thus:

$$S = \iint_{y,x} \sqrt{1 + \left( \frac{\partial f}{\partial x} \right)^2 + \left( \frac{\partial f}{\partial y} \right)^2} \, dA$$

where $dA$ is the area element in the $x$, $y$ plane and $f_x$ and $f_y$ are partial derivatives of $f(x,y)$ with respect to $x$ and $y$ respectively. In the case under consideration:

$$f(x,y) = \sqrt{R^2 - x^2 - y^2}$$
\[ f_x = \frac{-x}{\sqrt{R^2 - x^2 - y^2}} \quad f_y = \frac{-y}{\sqrt{R^2 - x^2 - y^2}} \]

and \(dA = r\,dr\,d\theta\)

Applying the rectangular to polar conversion, we obtain

\[ S = \int \int \frac{Rr}{\sqrt{R^2 - r^2}} \,dr\,d\theta \quad (7) \]

Now, as is apparent from Figure 39, the appropriate expression for \(r\) (equation (3) or equation (4)) to be used in equation (6) will depend upon whether the hatched area is bound by the sphere of the cylinder or both. Several cases are possible:

**CASE I** \( b = 0 \)

i. \( R \leq a \)

\[ S = 4\pi R^2 \]

In order to facilitate generalization, we rewrite it in the following form:

\[ S = 4R^2 \left\{ \pi - \int_{\pi/2}^{\pi/2} \sqrt{1 - \left(\frac{r_c}{R}\right)^2} \,d\theta \right\} \quad (8) \]

where the integral within the brackets is identically equal to zero.

ii. \( R > a \)

The hatched area is always bound by the cylinder. Therefore, \( r = r_c = a \), and
\[ S = 4 \int_{\theta = -\pi/2}^{\pi/2} \int_{r=0}^{Rt \sqrt{R^2-r^2}} \text{dr d} \theta \]
\[ = 4R \int_{-\pi/2}^{\pi/2} (-) \sqrt{R^2-r^2} \bigg|_{r=0}^{r_c=a} \text{d} \theta \]
\[ = 4R^2 \int_{-\pi/2}^{\pi/2} [1- \sqrt{1-(\frac{r_c}{R})^2}] \text{d} \theta \]
\[ = 4R^2 \left[ \pi - \int_{-\pi/2}^{\pi/2} \sqrt{1-(\frac{r_c}{R})^2} \text{d} \theta \right] \]
\[ S = 4R^2 \left[ \pi - \int_{-\pi/2}^{\pi/2} \sqrt{1-(\frac{r_c}{R})^2} \text{d} \theta \right] \quad (9) \]

**CASE II** \( 0 < b < a \)

i. \( 0 < R < (a-b) \): The sphere is contained inside the cylinder.

\[ S = 4\pi R = 4R^2 \left[ \pi - \int_{\theta = -\pi/2}^{\pi/2} \sqrt{1-(\frac{r_c}{R})^2} \text{d} \theta \right] \quad (8) \]

ii. \( (a-b) < R < (a+b) \): The sphere is bulging out on one side of the cylinder. Under this condition, \( r = r_s \) for \( -\pi/2 < \theta < \theta_x \) and \( r = r_c \) for \( \theta_x < \theta < \pi/2 \)

\[ S = 4 \left\{ \begin{array}{c}
\theta_x \quad R \\
\int_{\theta = -\pi/2}^{\pi/2} \int_{r_s=0}^{\sqrt{R^2-r^2}} \frac{Rr}{\sqrt{R^2-r^2}} \text{dr d} \theta + \int_{\theta = \theta_x}^{\pi/2} \int_{r_s=0}^{\sqrt{R^2-r^2}} \frac{Rr}{\sqrt{R^2-r^2}} \text{dr d} \theta \\
\end{array} \right\} \]
\[
\begin{align*}
S &= 4R \left[ \theta_x \sqrt{R^2 - r^2} \bigg|_{r=0}^{R} \pi/2 - (\theta_x - \pi/2) \int_{\theta_x}^{\pi/2} \sqrt{1 - \left(\frac{r_c}{R}\right)^2} \, d\theta \right] \\
&= 4R \left[ \int_{\theta_x}^{\pi/2} d\theta + \int_{\theta_x}^{\pi/2} (R - \sqrt{R^2 - r_c^2}) \, d\theta \right] \\
&= 4R^2 \left[ \theta_x - \pi/2 + \int_{\theta_x}^{\pi/2} \sqrt{1 - \left(\frac{r_c}{R}\right)^2} \, d\theta \right] \\
&= 4R^2 \left[ \theta_x - \pi/2 + \pi/2 - \theta_x - \int_{\theta_x}^{\pi/2} \sqrt{1 - \left(\frac{r_c}{R}\right)^2} \, d\theta \right] \\
&= 4R^2 \left[ \pi - \int_{\theta_x}^{\pi/2} \sqrt{1 - \left(\frac{r_c}{R}\right)^2} \, d\theta \right]
\end{align*}
\]

where \( r_c \) and \( \theta_x \) are given by the equations (5) and (6) respectively.

iii. \( R>(a+b) \): The off-centered sphere is bulging out on both sides of the cylinder. The hatched area is bound by the cylinder.

\[
S = 4R \int_{\theta_x}^{\pi/2} \sqrt{R^2 - r^2} \bigg|_{r=0}^{R} \, d\theta \\
&= 4R \int_{\theta_x}^{\pi/2} (-) \sqrt{R^2 - r^2} \bigg|_{r=0}^{R} \, d\theta \\
&= 4R \int_{\theta_x}^{\pi/2} (-) \sqrt{R^2 - r^2} \bigg|_{r=0}^{R} \, d\theta
\]
\[ S = 4R^2 \int_{-\pi/2}^{\pi/2} \left[ 1 - \sqrt{1 - \left(\frac{r_c}{R}\right)^2} \right] d\theta \]

\[ = 4R^2 \left[ \int_{-\pi/2}^{\pi/2} \sqrt{1 - \left(\frac{r_c}{R}\right)^2} d\theta \right] \]

**CASE III** \( b=a \)

i. Sphere totally contained inside the cylinder: non-existent.

ii. \( R<(a+b) \) or \( (a-b)<R<(a+b) \)

\[ S = 4 \left\{ \int_{\theta_x}^{\theta} R \frac{R}{\sqrt{R^2-r^2}} dr d\theta + \int_{r=0}^{0} \frac{R r}{\sqrt{R^2-r^2}} dr d\theta \right\} \]

\[ = 4R^2 \left\{ \int_{\theta_x}^{\theta} d\theta + \int_{0}^{0} \left\{ 1 - \sqrt{1 - \left(\frac{r_c}{R}\right)^2} \right\} d\theta \right\} \]

We notice that for \( 0<\theta<\pi/2 \), \( r_c \) is always zero. Therefore we could add the term:

\[ \int_{0}^{\pi/2} \left\{ 1 - \sqrt{1 - \left(\frac{r_c}{R}\right)^2} \right\} d\theta \]

Without changing the value of the integral, then

\[ S = 4R^2 \left\{ \int_{\theta_x}^{\theta} d\theta + \int_{0}^{0} \left\{ 1 - \sqrt{1 - \left(\frac{r_c}{R}\right)^2} \right\} d\theta \right\} \]
which is the same as equation (10). Hence

\[ S = 4R^2 \left[ \pi - \int_{\theta_x}^{\pi/2} \sqrt{1 - \left(\frac{r_c}{R}\right)^2} \, d\theta \right]; \quad r_c = 0 \text{ for } \theta > 0 \quad (14) \]

iii. \( R > (a+b) \)

\[
S = 4 \int_{\theta=\pi/2}^{\pi} \int_{r=0}^{r_c} \frac{Rr}{\sqrt{R^2 - r^2}} \, dr \, d\theta; \quad r_c = 0 \text{ for } \theta > 0
\]

Following the same reasoning as above; we can say

\[
S = 4 \int_{\theta=-\pi/2}^{\pi/2} \int_{r=0}^{r_c} \frac{Rr}{\sqrt{R^2 - r^2}} \, dr \, d\theta; \quad r_c = 0 \text{ for } \theta > 0
\]

This expression is the same as than in equation (12), hence

\[
S = 4R^2 \left[ \pi - \int_{\theta_x}^{-\pi/2} \sqrt{1 - \left(\frac{r_c}{R}\right)^2} \, d\theta \right]; \quad r_c = 0 \text{ for } \theta > 0 \quad (15)
\]

All these different cases can be represented by one general expression:

\[
S = 4R^2 \left[ \pi - \int_{\theta_x}^{\pi/2} \sqrt{1 - \left(\frac{r_c}{R}\right)^2} \, d\theta \right]
\]

where \( \theta_x \) for different cases is given by the following table:
<table>
<thead>
<tr>
<th></th>
<th>$R\leq (a-b)$</th>
<th>$(a-b)&lt;R&lt;(a+b)$</th>
<th>$R\geq (a+b)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$b=0$</td>
<td>$\pi/2$</td>
<td>--</td>
<td>$-\pi/2$</td>
</tr>
<tr>
<td>$b&lt;a$</td>
<td>$\pi/2$</td>
<td>equation (6)</td>
<td>$-\pi/2$</td>
</tr>
<tr>
<td>$b=a$</td>
<td>--</td>
<td>equation (6)</td>
<td>$-\pi/2$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$r_c=0$ for $\theta&gt;0$</td>
<td></td>
</tr>
</tbody>
</table>

and $r_c$ is given by the equation (5).
APPENDIX E

COMPUTER PROGRAM

LIBLIST,TIME=60,PAGES=10,STMTS=3000000,WORD

C THIS PROGRAM CALCULATES THE DOSE ABSORBED BY A RIGHT CIRCULAR CYLINDER OF RADIUS A FILLED WITH RADIOACTIVE FLUID_EMITTING C BETA PARTICLES

C VARIABLES USED IN THIS PROGRAM ARE THE SAME AS IN THE TEXT

1 REAL NU,NORM,KNORM,THETAX,INT1,INT2,INTF,INFD0Z
2 DIMENSION INT1(200),INT2(200),INTF(200),DCSEB(50),BCB(50)
3 DIMENSION RADIUS(200),S(200),RATIO(200),THETAX(200),PHD0ZB(50)
4 READ (5,1) A,EAVG,EGA,V,EMAX
5 PI=3.14159
6 TOL=0.0001
7 DELA=0.20
8 DEL=0.02
9 DELT=2.0/57.2958
10 NU=1.6*2.0*(EAVG/EGA)**0.36*1.37
11 P=1.25-0.954*ALOG(EMAX)
12 BMAX=0.412*(EMAX**1.0)

C KNORM IS THE NORMALIZATION CONSTANT

13 KNORM=169.867*(EAVG*(NU**3.0)/((3.0-((1.0-NU*RMAX)**2.0))**1.*1.0-NU*RMAX))
14 NORM=4.0*(KNORM/(NU**2.0))
15 N=1.5
16 NR=(RMAX/DEL)**1.5
17 R=0.00

C EVALUATION OF DOSE RATE AS A FUNCTION OF DISTANCE FROM A POINT SOURCE

18 DO 10 H=1,NR
19 ALPHA=ALPHA*(1.0-HD*EXP(1.0-NU*R))
20 IF((NU*R),.GE.1.0) ALPHA=0.0
21 INT1(N)=INT1(N)+ALPHA*NU*R*EXP(1.0-NU*R)-NU*RMAX*EXP(1.0-NU*RMAX)
22 IF(NU**,NR) INT1(N)=0.0
23 10 R=R+DEL
24 INFD0Z=2134.62*EAVG

C INFDOZ IS THE TOTAL ENERGY ABSORBED IN RADS PER HOUR BY A FLUID ELEMENT IN AN INFINITE RESERVOIR OF ACTIVITY 1 MILLICURIE/ML.

C WRITE (6,2)

C FORMAT STATEMENTS 2 AND 21 DISPLAY FRACTION OF THE TOTAL Emitted DOSE ABSORBED BY THE CYLINDER OF RADIUS A

C WRITE (6,5) A

C FORMAT STATEMENTS 3 AND 31 DISPLAY DOSE RATE AT ANY POINT INSIDE THE CYLINDER LOCATED AT A DISTANCE B FROM THE AXIS

26 DELB=(A/20.0)
27 B=0.0
28 DO 55 K=1,21
29 WRITE (6,4) A,B

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FORMAT STATEMENTS 4 AND 41 DISPLAY THE FRACTION OF A SPHERE OF
RADIUS R CONTAINED INSIDE A CYLINDER OF RADIUS A.

R=0.0
DO 45 I=1, NR
RADIUS(I)=R
IF((R-(A-B)) .LE. TOL) GO TO 15
GO TO 20
15 S(I)=4.0*D1*R**2.0
RATIO(I)=1.0
THETA(I)=PI/2.0
AOUT=0.0
GO TO 40

20 IF((R-.GE. (A+B)) ) GO TO 25
ARG=(A**2-B**2-R**2)/(2.0*B*R)
IF(ARG.LE.(-1.0)) ARG=1.0
THETA(I)=ARCSIN(ARG)
GO TO 30

25 THETA(I)=(PI/2.0)*(-1.0)

30 RANGE=(((PI/2.0)-THETA(I))/DELT
MT=MT+0.5
NTM=NTM-1
DO 35 J=1, NR
X=THETA(I)+PI/DELT
AOUT=AOUT+F(R,A,B,X+T0V2)
35 AOUT=4.0*R**2.0*(PI-AOUT)
HALF=HALF+F(R,A,B,THETA(I)+T0V2)
BA T(I)= (PI-AOUT)/PI
INT2(I)=INT1(I)*INT2(I)
R=R+DELP

C EVALUATION OF DOSE RATE AT POINT B

FULLR=0.0
HALFB=INTF(2)
DO 50 J=3, NR+2
FULLR=FULLR+INTF(L)
50 FULLR=FULLR+INTF(L+1)

DOSEB(K)=(DELB*NORM/3.0)*(INTF(1)+4.0*HALFB+2.0*FULLB+INTF(NR))

PBDOZB(K)=DOSEB(K)/DOSEB(1)

BDB(K)=B*DOSEB(K)
WRITE (6,41) (RADIUS(I), RATIO(I), INTF(I), I=1, NR)
WRITE (6,31 )B, DOSEB(K), PBDOZB(K)

AVGDOZ=((2.0*DELB)/(3.0*A**2)) *(BDB(1)+4.0*HALFB+2.0*FULLB+BDB(21))

PHIA=AVGDOZ/INFDOZ
WRITE (6,21 ) A, AVGDOZ, PHIA

C EVALUATION OF DOSE ABSORBED BY THE CYLINDER

FULLB=0.0
HALFB=INTF(2)
DO 60 M=3,19,2
FULLB=FULLB+INTF(M)

AVGDOZ=((2.0*DELB)/(3.0*A**2)) *(BDB(1)+4.0*HALFB+2.0*FULLB+BDB(21))

PHIA=AVGDOZ/INFDOZ
WRITE (6,21 ) A,AVGDOZ, PHIA

C 2 FORMAT(4F10.4)
C 2 FRACTIONAL DOSE RATE*,/5X,*RADIUS OF THE CYLINDER*,5X,*AVERAGE DOSE RATE*,5X,*
### FUNCTION F(R,A,B,T)

```fortran
FUNCTION F(R,A,B,T)
  IF (B.EQ.A .AND.T.GE.0.0) GO TO 70
  ADBCOST=A**2-(B*COS(T))**2
  IF(ABDLCOST.LT.0.0) ADBCOST=0.0
  HC=SQRT(1.0-ABDLCOST)-B*SIN(T)
  IF((HC/RC).GE.1.0) GO TO 80
  RC=0.0
  F=SQRT(1.0-(RC/RC)**2.0)
  RETURN
END
```

### Sample Output

<table>
<thead>
<tr>
<th>Radius of Cylinder (cm)</th>
<th>Offset from Center (cm)</th>
<th>Total Dose at Point B (u.u.)</th>
<th>Fractional Dose</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>0.00</td>
<td>1416.9</td>
<td>1.000</td>
</tr>
<tr>
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<td>0.02</td>
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</tr>
<tr>
<td>0.03</td>
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<tr>
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</tr>
<tr>
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<td>0.20</td>
<td>660.8</td>
<td>0.471</td>
</tr>
</tbody>
</table>

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VITA

EXAMINATION AND THESIS REPORT

Candidate: Satyajit Verma
Major Field: Chemical Engineering
Title of Thesis: Effect of Capillary Diameter on the Rate of Radiation Induced Polymerization of Acrylamide in Saline Solutions Containing Dissolved $^{32}$P

Approved:

[Signatures]

Major Professor and Chairman
Dean of the Graduate School

EXAMINING COMMITTEE:

[Signatures]

Date of Examination: November 25, 1980