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## An X-Ray Study of Cluster Formation in Liquid Mixtures

Daniel K. Sorgen

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AN X-RAY STUDY OF CLUSTER FORMATION IN LIQUID MIXTURES

by

Daniel K. Sorgen

B.A. in Physics, Concordia College 1964

A Thesis

Submitted to the Faculty

of the

University of North Dakota

in partial fulfillment of the requirements

for the Degree of

Master of Science

Grand Forks, North Dakota

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This thesis submitted by Daniel K. Sorgen in partial fulfillment of the requirements for the Degree of Master of Science in the University of North Dakota, is hereby approved by the Committee under whom the work was done.

Harold D. Bale  
Chairman

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## ABSTRACT

Other workers have attributed the anomalous absorption of ultrasonic waves in certain liquid mixtures as being due to the formation of molecule clusters. A study was performed on two binary liquid mixtures employing small angle scattering of x-rays. Water-tertiary butanol mixtures and ethanol-glycerin mixtures were each studied in various concentrations.

The scattered intensity was measured as a function of scattering angle. Certain necessary corrections on the raw data were performed. Using this corrected data a Guinier plot was made for each solution studied. From the Guinier plot it was possible to determine a radius of gyration for the clusters in each sample. A plot of the radius of gyration vs concentration was made for each of the two systems studied.

It was found that molecular cluster formation apparently does take place in the mixtures and that the size of the clusters varies with concentration, with a maximum radius of gyration at an intermediate concentration.

## INTRODUCTION

Liquids have neither a calculable periodicity as do crystals nor do they have the random character of gases, hence the detailed study of their diffraction of x-rays presents certain difficulties. However, advancement of knowledge of the structure of substances in the liquid state has been gained by studies of this kind. For many years the large angle liquid diffraction technique has been used to determine first and second nearest neighbor distances.<sup>1</sup> Molecular cluster formation in certain liquids has been studied by means of small angle scattering of x-rays.<sup>2</sup> At small angles the scattering is related to the existence of fluctuations of density in the sample, the scattering depending on the form and size of the regions of different density. By making a theoretical interpretation of the small angle scattering curve one can hope to obtain information regarding the size of the scattering region.

In curves of ultrasonic absorption as a function of concentration, absorption maxima have been observed at an intermediate concentration in systems of binary liquid mixtures. Most of these systems have water as a component; some others are formed by alcohols. Willis<sup>3</sup> obtained strong absorption peaks at intermediate concentrations in a mixture



of acetone with water and ethyl alcohol with water, while Sette<sup>4</sup> has observed an absorption maxima at an intermediate concentration in systems of nitrobenzene and an alcohol. C. J. Burton<sup>5</sup> found absorption peaks at intermediate concentrations in mixtures of water with ethanol, propanol, isopropanol, and tertiary butanol and observed that the magnitude of the absorption peak increased with increasing molecular volume of the organic constituent (i.e., ethyl to butyl), and there was also a simultaneous shift of the position of the maximum toward lower alcohol concentrations. The magnitude of the absorption peak of the tertiary butanol system was  $10^{15} \frac{\alpha}{v^2} \cong 38$ , as compared with a value of  $10^{15} \frac{\alpha}{v^2} \cong 6$  for pure organic liquid.

Anantaraman<sup>6</sup> and his associates have observed absorption maxima at intermediate concentrations of mixtures of nitrobenzene and iso-octane near the critical point. Absorption maxima in mixtures of ethyl alcohol and water were observed at intermediate concentrations by Storey<sup>7</sup> who suggested that the anomalous absorption may be due to the interaction between the molecules of the two components, leading to the partial development of a molecular complex in the liquid.

Sette<sup>8</sup> believes that an explanation of this behavior may be found by the presence of the formation of molecular clusters. Clusters of different compositions are present so the solution is no more a homogeneous phase. In addition

to the normal classical absorption, there are two other ways by which the presence of clusters can produce an increase of absorption. One way is through relaxation phenomena. The second way in which clusters can produce ultrasonic absorption is due to the fact that when density fluctuations are present in a liquid the losses produced by viscosity increase.

Andraea<sup>9</sup> and his coworkers have studied ultrasonic absorption in aqueous solutions of non-electrolytes. They analyzed experimental data of ultrasonic absorption in terms of the relaxation of chemical equilibria involving molecules of water, of solute and of complexes of water and solute. Four theoretical models were used in their analysis and they suggested that a satisfactory model would incorporate features of each one. Andraea et al. concluded for non-electrolytes dissolved in water that as the concentration of the solute is increased from zero, there is a breakdown of the water structure and that it seems probable that each solute molecule prevents by its shape and size a number of water molecules around it from maintaining hydrogen bonded contact with the highly oriented water structure nearby. These 'free' water molecules will pack closely around the solute molecule. With further increase in concentration of the solute the water complexes begin to give rise to ultrasonic absorption. This increases to a maximum at the peak

sound absorption concentration and then falls again as the amount of water available becomes a limiting factor.

As stated in the next section scattering from particles in a solution can be considered as scattering from particles of density equal to the difference of the densities of the two constituents of the solution. Consideration was therefore given to mixing two liquids that would give a large density difference and to observe the scattering from clusters in the solution, if any were formed. Ethanol and glycerin were chosen as the two constituents and were mixed in various concentrations.

The purpose of this investigation is to study the small angle scattering from two different liquid mixtures. Water-tertiary butanol and ethanol-glycerin mixtures are each studied in various concentrations. Any dependence of the size of the clusters on the concentration will then be determined. In the case of the water-tertiary butanol mixtures the concentration size dependence of the clusters determined by x-ray methods will be compared with the effects observed by ultrasonic methods.

## THEORY

A complete discussion of the theory and applications of small angle scattering is given in Guinier and Fournet.<sup>10</sup> Only the more general theoretical concepts and results which are applicable to analysis of the data obtained from the solutions studied in this investigation will be reviewed.

Debye developed a mathematical expression for the scattered intensity from a particle: 
$$I(h) = \sum_i \sum_j f_i f_j \frac{\sin hr_{ij}}{hr_{ij}}$$

where  $h = 4\pi \sin \theta / \lambda$ ,  $\lambda$  = the wave length of the x-rays,  $f_i$  and  $f_j$  are the respective atomic scattering factors of the  $i^{\text{th}}$  and  $j^{\text{th}}$  atoms and  $r_{ij}$  is the magnitude of the vector separating these two atoms. All orientations of the system are assumed equally probable. For a system of  $n$  identical randomly arranged particles the scattering will be  $n$  times the scattering for one particle. If the particle has a center of symmetry the expression for the scattered intensity can be given as  $I(h) = I_e(h) F^2(h)$  where  $I_e(h)$  is the scattered intensity due to a single electron and  $F(h)$  is the particle structure factor. In solutions the particles are in motion so one observes an average intensity:  $\overline{I(h)} = I_e(h) \overline{F^2(h)}$

where 
$$\overline{F^2(h)} = \sum_i \sum_j f_i f_j \frac{\sin hr_{ij}}{hr_{ij}}$$

The expression for  $\overline{F^2(h)}$  can be expanded in a power series, retaining only the first two terms. This power series expansion leads to an expression which can be written in terms of the electronic radius of gyration of the particle about its electronic center of mass:

$$I(h) = n^2 e^{-\frac{h^2 R_g^2}{3}}$$

where  $n$  is the total number of electrons in the particle and  $R_g$  is called the electronic radius of gyration. If this Gaussian approximation is valid throughout most of the very small angular region the plot of the  $\log I(h)$  vs  $h^2$  curve or Guinier plot should be a straight line in this region. From the slope of this curve at zero angle the radius of gyration of the particle can be calculated. The size of the angular region through which the straight line portion of the curve will extend and the lower angular limit of the data available will determine the accuracy of the radius of gyration calculation since the slope at zero angle is the desired slope necessary in the calculation and this slope must be found by extrapolation of the curve to zero angle. The calculation of the radius of gyration does not make any assumptions regarding particle shape or uniformity of particle density. No slit-height corrections are required for the

radius of gyration calculation if the intensity curve is a Gaussian over much of the small angle region.<sup>11</sup>

Theoretically, scattering is dependent on the product  $hR$  where  $R$  is the radius of the particle, hence, it follows that the scattering from identically shaped particles falls off more rapidly as the particle size increases. Because of this it is found, when comparing the scattering curves of two solutions, that the curve which exhibits the most rapid decline in intensity with increasing angle is the curve from the solution that contains the larger particles.

In the above theoretical interpretation it is assumed that the particles are suspended in a vacuum. In order to apply these ideas to particles suspended in solutions the scattering from the medium surrounding the particles must be accounted for. Assuming the particles are suspended in a homogeneous medium of electronic density  $p_0$ , the scattering body can be considered as the superposition of a continuous medium of density  $p_0$  and the particles of density  $p-p_0$ . Established theory will thus apply if the observed scattering is attributed to particles of density  $p-p_0$ .<sup>12</sup>

The zero angle intensity is proportional to the number of scattering centers, to the square of the mass,  $m$ , of the particles and to the transmission of the sample. From this value  $m$ , proportional to the mass of the particles, can be obtained by dividing the zero angle intensity by

the concentration and the transmission. This value, proportional to the mass, serves as a check on the concentration size dependence of the particles which was determined from the slope of the Guinier plots.

## EXPERIMENTAL EQUIPMENT

The experimental equipment consisted of a power supply, two x-ray sources, a diffractometer and a detection system. A copper target x-ray tube was used with the water-tertiary butanol mixtures and was operated at 23 kv and 12 ma tube current. A molybdenum target x-ray tube operated at 25 kv and 12 ma was used in obtaining scattering curves for the ethanol-glycerin mixtures. The diffractometer employed four slits of adjustable widths spaced at fifty centimeter intervals. The scattering sample was placed midway between the second and third slits and was directly above the axis of rotation of the collimator arm. The slit assemblies were housed in two 1 3/8 in. diameter brass tubing sections which were evacuated by means of a Duo-Seal vacuum pump. The area in the immediate vicinity of the sample was not evacuated when the molybdenum target x-ray tube was used. However, due to the reduced intensity of the copper radiation, when the copper target x-ray tube was used the brass tubing sections were each connected by means of flexible hoses, to a chamber in which the sample holder was housed. The whole system was then evacuated to reduce absorption and scattering of the x-rays by air.



The pivot arm was controlled by a tangent screw arrangement that allowed selections of the scattering angle to within 0.0001 radians. All slits were adjusted to 0.060 in. when using the molybdenum tube and were set at 0.030 in. when the copper tube was used.

The detection system consisted of a Phillips Norelco pulse height analyzer-timer-amplifier coupled with a Tracerlab scaling unit. To these units was connected either a Phillips Norelco proportional counter or a Phillips Norelco scintillation counter mounted at the final slit of the diffractometer. The proportional counter was used with the copper target x-ray tube and the scintillation counter was used in detecting radiation from the molybdenum tube. Since the pulse height analyzer allowed discrimination of the pulses coming from the counter, it eliminated pulses due to noise and background radiation.

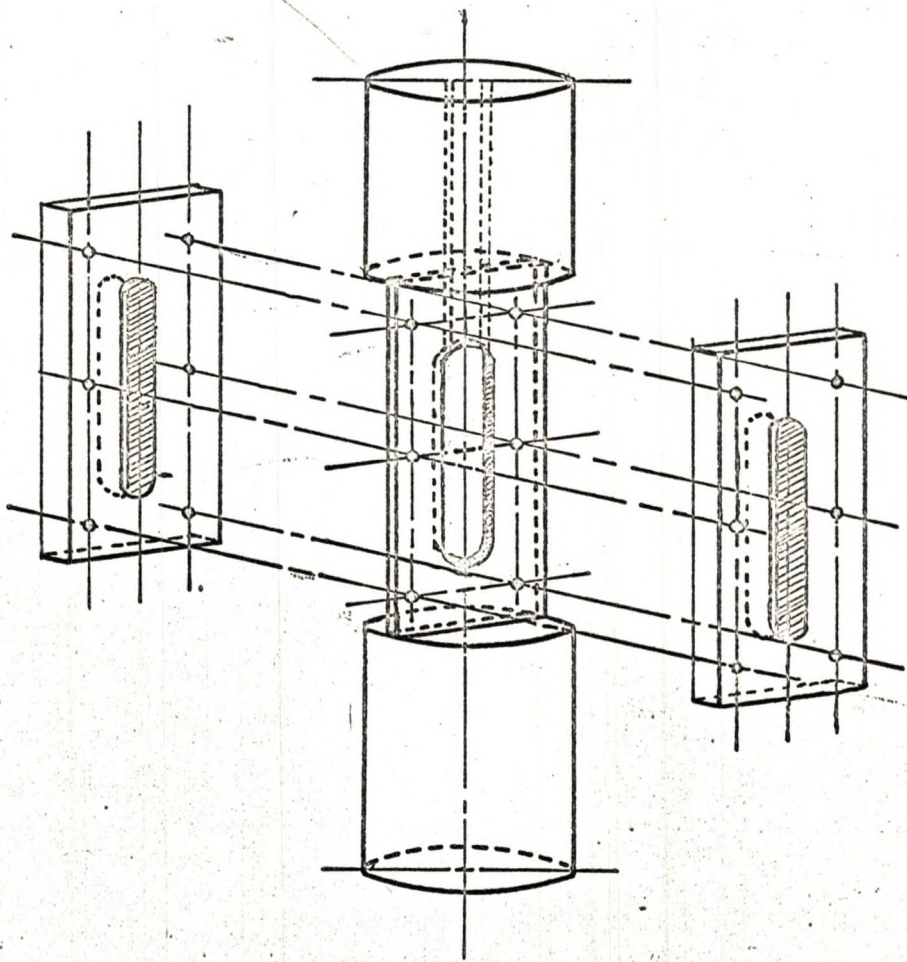
The sample holders for the ethanol-glycerin mixtures were made from  $3/8$  in. aluminum stock. A slot  $1/4$  in. by 1 in. was milled in each sample holder to accommodate the sample. Windows were made of Saran Wrap and were bonded to the sample holder with Duro Epoxe cement. The sample was introduced into the sample holder by means of a  $1/8$  in. hole drilled through the top of the sample holder into the slot. The sample holder was held in place in the diffractometer by a brass fitting which was placed in a brass

adapter centered over the axis of rotation.

The sample holders used for the water-tertiary butanol mixtures were made from 1 in. brass rod as shown in Plate I. The optimum thickness of the sample was obtained by milling a region 1 in. high on opposite sides of the rod leaving a section 0.060 in. in thickness. A space for the sample solutions was provided by machining a  $3/16$  in. by  $7/8$  in. slot through the section, parallel to the height of the section. The windows of the sample were cut from mica and were approximately 0.001 in. thick. Attempts were made to use both Saran Wrap and Mylar as sample holder windows, however, more scattering was observed from these materials than from the mica. Both windows were sealed to the sample holder with Dow Corning stopcock grease and were held in place by flanges on both sides of the sample holder. These flanges were made from  $1/4$  in. thick brass stock. The sample was introduced into the sample holder by means of two 0.040 in. holes drilled through the top of the sample holder into the slot. The sample holder was inserted into the evacuation chamber, centered over the axis of rotation.

Legend for Plate I on reverse side  
Sample holder

Plate I  
Legend for Plate I on reverse side  
**Sample holder**



## MATERIALS AND SAMPLE PREPARATION

Practical grade tertiary butanol,  $(\text{CH}_3)_3\text{COH}$ , was mixed with distilled water to prepare solutions of 0.075, 0.11, 0.16, 0.20, 0.30, and 0.040 mole fraction tertiary butanol, each with a volume of 10 ml. These solutions were used without further purification. They also were prepared and used at room temperature. The mole fraction concentration was mixed in terms of volume. The mole fraction is defined as the number of molecules of solute divided by the total number of molecules in solution, i.e.,

$$n = [P_1 V_1 / (\text{mole wt.})_1] / [P_1 V_1 / (\text{mole wt.})_1 + V_2 / (\text{mole wt.})_2]$$

where the subscript 1 refers to the density, volume and molecular weight of tertiary butanol, the subscript 2 refers to the volume and molecular weight of water and  $n$  is the mole fraction. The solutions were stored in test tubes with cork stoppers. Concentrations of 0.025 and 0.050 mole fraction were also prepared but the small angle scattering from these two mixtures was too weak to provide a reliable scattering curve, therefore, these solutions were not investigated further.

Absolute ethanol was mixed with U.S.P. grade glycerin

in preparing solutions of 20, 25, 28.5, 30, 35, 40, 45, and 50 percent glycerin by volume and no attempt was made at further purification. Each solution had a total volume of 10 ml. These solutions were prepared and stored at room temperature. In each of the two mixtures, the two constituent liquids are miscible in all proportions. Neither mixture is known to have a critical temperature for solubility.

## PROCEDURE

The molybdenum target x-ray tube was used to measure the scattered intensity of the ethanol-glycerin mixtures at a series of scattering angles. The number of counts taken at each of the selected angles was 3000. Measurements were made at ten positions of scattering angle which varied from 0.0073 radians to 0.0648 radians. The consistency of the beam was checked by observing the scattering from a reference  $\text{SiO}_2$  gel sample. This reference sample was also used to determine the transmission of each sample by measuring the scattered intensity, at the reference angle, of the  $\text{SiO}_2$  gel alone and with the sample. Scattering curves were also obtained for pure samples of the ethanol and the glycerin. These were used to calculate a correction factor in an attempt to eliminate background scattering. After determining the corrected intensity, a Guinier plot was made for each concentration.

Using the copper target x-ray tube, the experimental scattered intensity,  $I$  (counts/sec), for the water-tertiary butanol mixtures, was measured at a series of scattering angles,  $(2\theta)$ , to determine the  $I$  vs  $(2\theta)^2$  curve. The range of angles over which a Guinier plot is valid decreases with



increasing particle size. Small angles correspond to small values of  $h$  which can be obtained by using radiation of longer wave length. Therefore, in investigating the water-tertiary butanol mixtures, copper radiation, which has a wavelength approximately twice that of molybdenum radiation, was used since the particle sizes in these mixtures were larger than those in the ethanol-glycerin mixtures. The number of counts taken at each of the selected angles was 1000. The probable error was approximately 3 per cent.<sup>13</sup> Measurements were made at six positions of scattering angle varying from 0.0062 radians to 0.0112 radians. The small angle patterns were obtained at least twice using first samples from solutions that were at least a month old. Fresh solutions were then made and scattering curves were obtained for a sample of each solution to determine whether there was any change in the scattering pattern due to aging. The fresh solutions verified the results of the aged ones since for each concentration studied no noticeable difference in scattering due to aging, was observed. Since there was no noticeable difference in the two samples studied, for each concentration the sum of the two was used to make the final Guinier plot. At the end of each run, the scattered intensity at the first point of the run was measured again to give an indication of the consistency of the incident beam with time. Portions of the scattering curves were also

retaken at intervals throughout a run to determine the extent of any long term drift in the intensity of the main beam. However, such a drift was found to be negligible over the period of a run.

Scattering curves were also obtained for the empty sample holder in an attempt to determine a more accurate scattering from the molecular clusters in the sample by subtracting the scattering from the mica windows. Except for the smallest angle, the scattering from the mica windows was found to be constant. The slightly higher intensity at the smallest angle was thought to be due to its proximity to the edge of the main beam. The transmission was assumed to be approximately 25 per cent so one-fourth of the scattering from the empty holder at the smallest angle was subtracted from the scattering of each of the samples at the smallest angle. This was the only correction factor employed since the rest of the scattering from the empty sample holder was constant and minimal. This method was used to obtain the Guinier plots for each of the samples.

## RESULTS AND CONCLUSIONS

Experimental small angle scattering curves were taken from eight solutions of ethanol-glycerin mixtures which varied in concentration. Scattering curves were also taken for samples of pure ethanol and pure glycerin in an attempt to derive a correction factor due to the background scattering. The correction factor at each scattering angle was the sum of two terms: the percentage of ethanol in the sample times the intensity from pure ethanol at the angle considered times the transmission of the sample divided by the transmission of the pure ethanol; the other term was the percentage of glycerin in the sample times the intensity from pure glycerin at the angle considered times the transmission of the sample divided by the transmission of the pure glycerin. The sum of these two terms was used as the correction factor at each angle which was thus subtracted from the measured intensity to obtain the corrected intensity at each scattering angle. Measurement of the scattered intensity from the empty sample holder was made but was not employed as a correction factor since it was very small compared with the scattering from the sample itself. It was also necessary to take scattering curves from the pure ethanol and the pure glycerin to determine if the scattered

intensity from the mixtures was greater than the scattering from both the constituents alone to see if any clusters were present. The scattering from the mixtures was greater than that from either of its constituents. The scattering from the mixtures also decreased continually with increasing scattering angles so did not have the general form of ordinary liquid scattering as did the pure ethanol and the pure glycerin.

A Guinier plot was then made for each sample investigated. The results are shown on Plate II through Plate V. The radius of gyration was then calculated from each Guinier plot by multiplying the square root of the slope by 0.296, the constant being determined by the fact that molybdenum radiation was used. The results are shown in Table I. The radius of gyration for the particles ranges from 3.64 Angstroms for the 20 per cent solution through a maximum of 3.99 Angstroms for the 30 per cent solution and then decreases to a value of 3.82 Angstroms for the 50 per cent solution. As seen from the Guinier plots the zero angle intensity also is a maximum for the 30 per cent solution with a continual decrease as the solution concentration proceeds to higher and lower concentrations.

It was also desired to determine the approximate size of a molecule in a sample of pure glycerin so as to make a comparison with the radius of gyration of the par-

ticles that were doing the scattering in the various mixtures. The molecules were assumed to be spheres for this calculation. The radius was calculated from the expression

$$r = \sqrt[3]{3(\text{mole wt.})/4\pi N_0 \rho}$$

where  $r$  is the radius of the molecule,  $N_0$  is Avagadro's number and  $\rho$  is the density of glycerin. This gives the result that  $r = 3.05$  Angstroms, which is less than the results obtained for the radius of gyration of the particles in the mixtures. The fact that the calculated radius of the particle was smaller than the experimental radius of gyration together with the fact that the scattered intensity from the ethanol-glycerin mixtures was greater than the scattered intensity from either ethanol or glycerin alone, brought the conclusion that clusters were formed in the mixtures. These clusters appear to have a maximum radius of gyration at an intermediate concentration. In Plate VI the radius of gyration is plotted as a function of concentration, the value at 100 per cent glycerin being the value of the radius of a molecule of glycerin calculated above.

Experimental small angle scattering curves were also taken from six solutions of water-tertiary butanol mixtures which varied in concentration from 0.075 to 0.40 mole fraction tertiary butanol. Scattering curves were also taken from samples of distilled water, pure tertiary butanol and from the empty sample holder in an attempt to determine

a background correction factor to determine whether or not clusters were formed. Except for the smallest angle the scattered intensity from the pure samples of water and of tertiary butanol was very small and was also constant over the range of angles studied, as was the scattered intensity from the empty sample holder. The scattered intensity from the mixtures of water and tertiary butanol was found to be much greater than that from pure samples of either of the constituents. It was therefore concluded that cluster formation did take place. As stated previously, the slightly increased intensity at the smallest angle was found to be due to the proximity of the counter to the main beam. The only correction factor employed was to correct for this effect at the smallest angle.

Except for the 0.075 mole fraction solution, two solutions of each concentration were examined and their sum was used in making a Guinier plot. A Guinier plot for each concentration is shown on Plate VII and Plate VIII. The radius of gyration was then calculated for each mixture from its Guinier plot by multiplying the square root of the slope by 0.645 where the constant was determined by the fact that copper radiation was used. The results are shown in Table II. A value  $m$ , proportional to the mass of the scattering particle and determined from the zero angle intensity is also given in Table II for each concentration. This value

was found to depend upon the concentration in the same manner as does the radius of gyration. Since  $m$  is proportional to the mass and  $R_0$  is proportional to the size of the particle, the value of  $\sqrt[3]{m}/R_0$  should be constant for all solutions. In Table II it is seen that, except for the two solutions of greatest tertiary butanol concentration, this value is approximately constant. The radius of gyration for the clusters ranges from 21.7 Angstroms for the 0.075 mole fraction solution to a maximum of 23.4 Angstroms for the solution of 0.11 mole fraction concentration and decreases to a value of 19.9 Angstroms for the 0.4 mole fraction solution.

Solutions of .025 and .050 mole fraction were not examined because they gave very weak scattering. The very weak scattering from these samples was probably due to the fact that fewer scattering centers were present in these solutions than in the solutions of higher concentration. The weak intensity was also due to the increased absorption of the water in these solutions since they each had a high water content.

Burton's results for ultrasonic absorption in mixtures of water and tertiary butanol as a function of concentration are shown in Plate IX. He obtained a maximum absorption value at 0.11 mole fraction tertiary butanol. A plot of radius of gyration vs concentration is shown on

Plate X. There is a maximum for the radius of gyration at a concentration of 0.11 mole fraction tertiary butanol. The general shape of this curve corresponds to the shape of Burton's curve for ultrasonic absorption which implies that from this data the increased ultrasonic absorption in mixtures of water and tertiary butanol may be due to an increase in the size of the clusters.

It has been shown that cluster formation apparently does occur in mixtures of ethanol and glycerin with a maximum radius of gyration at an intermediate concentration. In the ethanol-glycerin system, the size of the clusters apparently does depend upon the concentration of the solution. It has also been shown that cluster formation does occur in mixtures of water and tertiary butanol and that size of the clusters in the mixtures varies with the concentration in the same manner as does the ultrasonic absorption. It has also been shown that the value proportional to the mass of the clusters, which was calculated from the zero angle intensity, also varies with the concentration in the same manner as do the radius of gyration and the ultrasonic absorption.



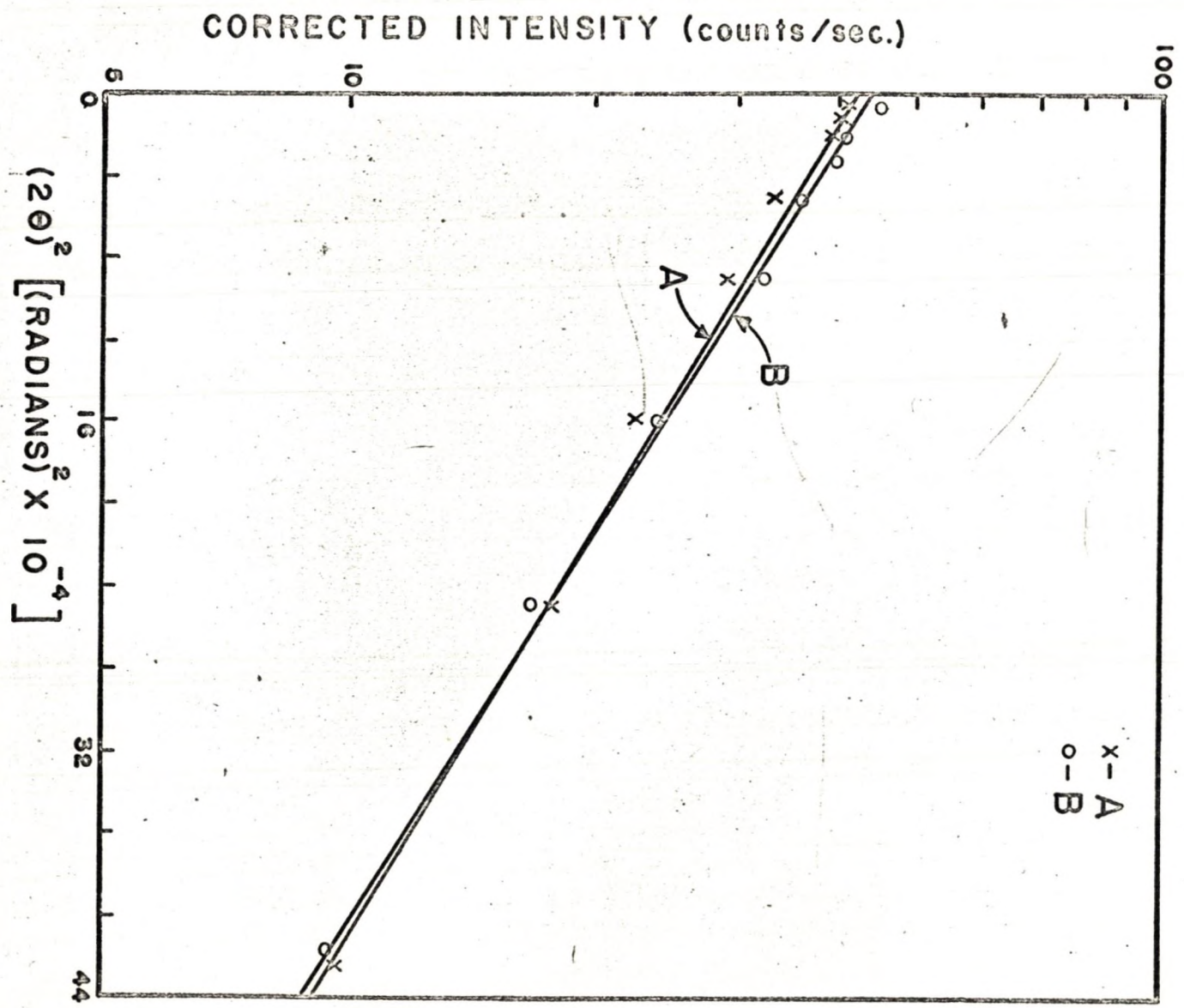
Plate II  
**Legend for Plate II on reverse side**

Plate II

off: curve of ... ..

Guinier plot

Guinier plot of two ethanol-glycerin solutions.  
A,  $R_0 = 3.64$  Angstroms, Concentration = 20 per cent glycerin  
by volume; B,  $R_0 = 3.70$  Angstroms, Concentration = 25 per  
cent glycerin by volume.

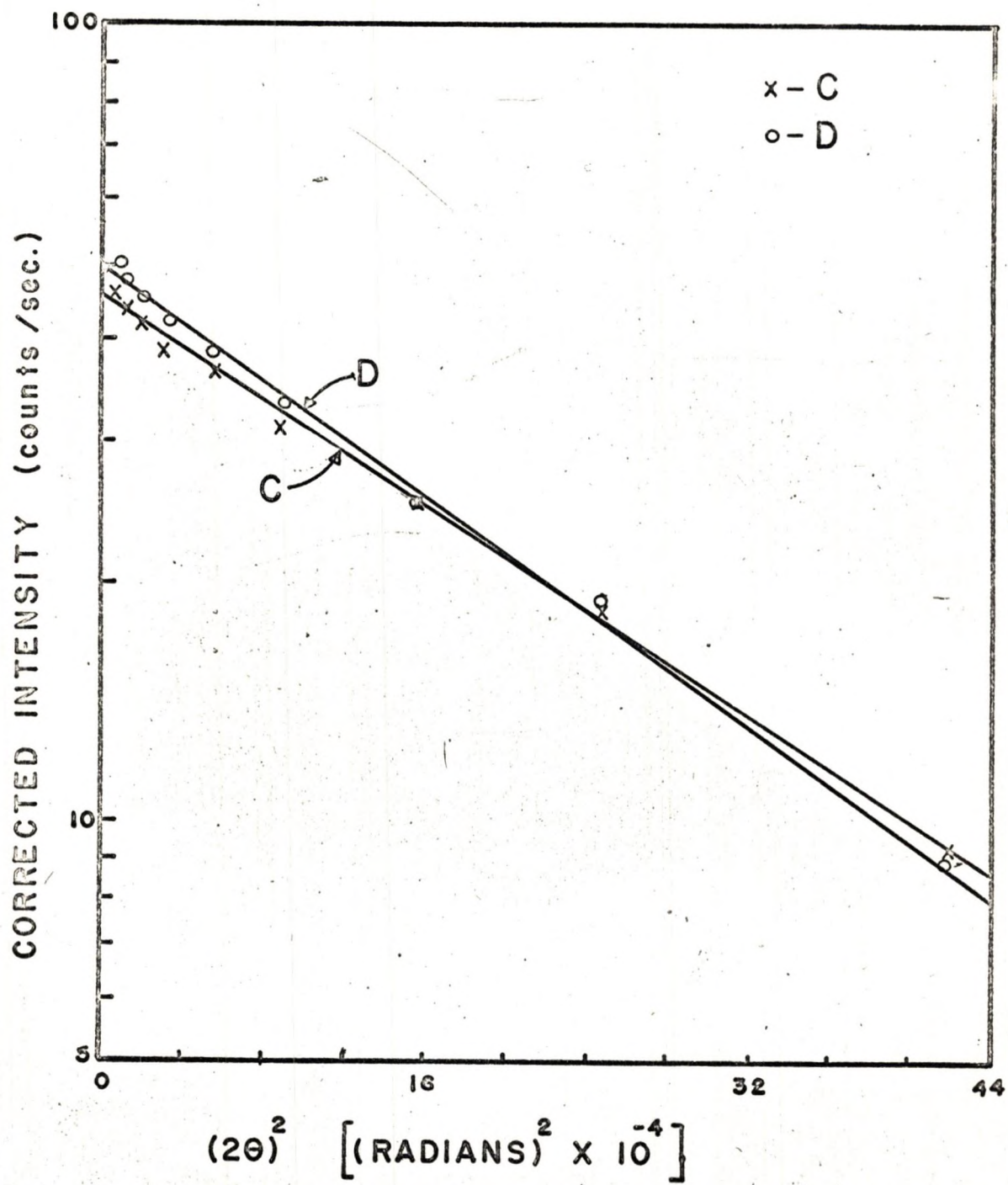


III 01651  
Legend for Plate III on reverse side

Plate III

Guinier plot

Guinier plot of two ethanol-glycerin solutions.  
C,  $R_0 = 3.79$  Angstroms, Concentration = 28.5 per cent  
glycerin by volume; D,  $R_0 = 3.99$  Angstroms, Concentration =  
30 per cent glycerin by volume.



Legend for Plate IV on reverse side

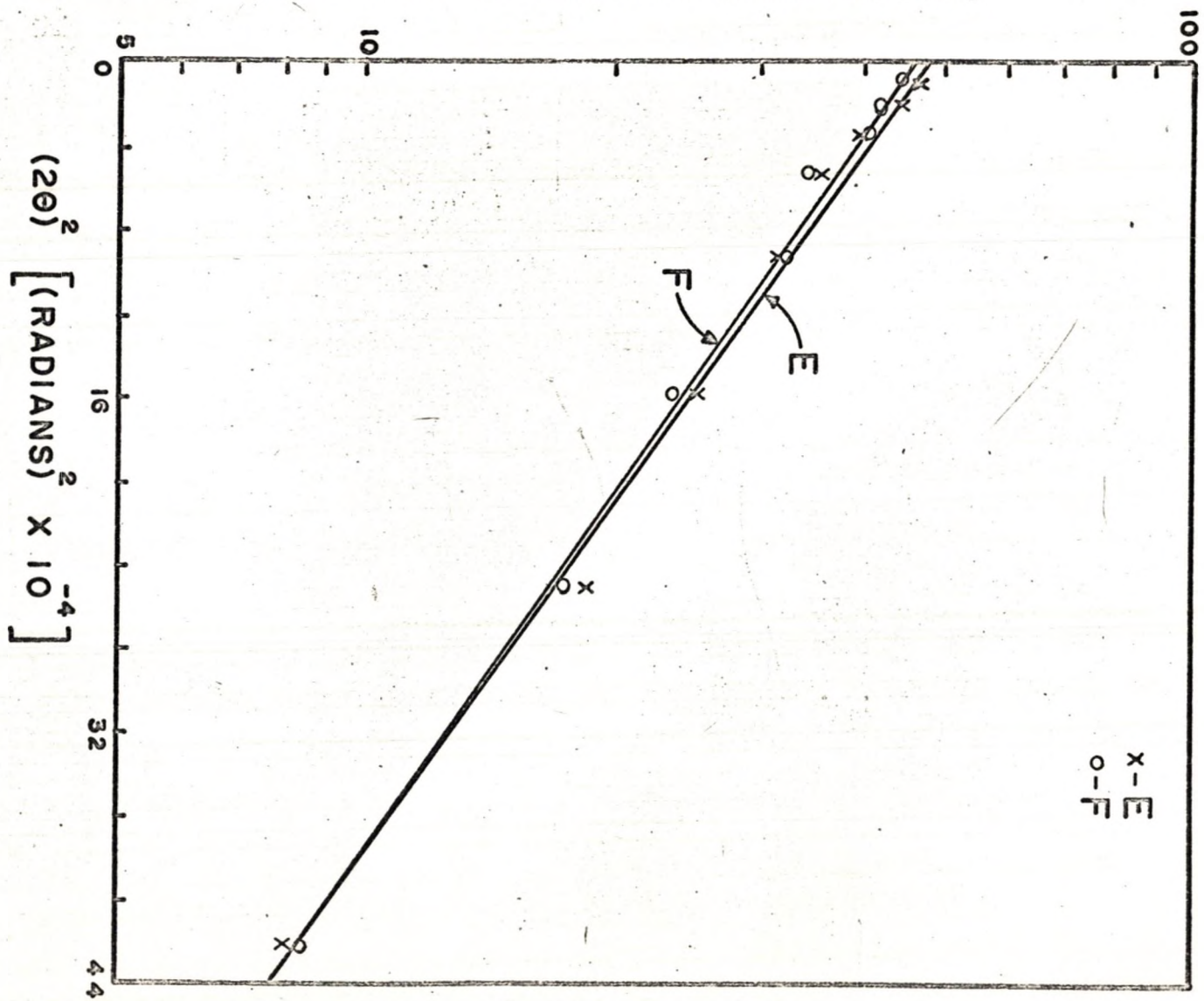
Plate IV

Guinier plot

Guinier plot of two ethanol-glycerin solutions.  
E,  $R_0 = 3.95$  Angstroms, Concentration = 35 per cent glycerin  
by volume; F,  $R_0 = 3.93$  Angstroms, Concentration = 40 per  
cent glycerin by volume.



CORRECTED INTENSITY (counts/sec.)



V. 1919  
**Legend for Plate V on reverse side**  
to be printed

## Plate V

obla erover n... tol enoged

## Guinier plot

Guinier plot of two ethanol-glycerin solutions.  
G,  $R_0 = 3.88$  Angstroms, Concentration = 45 per cent glycerin  
by volume; H,  $R_0 = 3.82$  Angstroms, Concentration = 50 per  
cent glycerin by volume.

CORRECTED INTENSITY (counts /sec.)

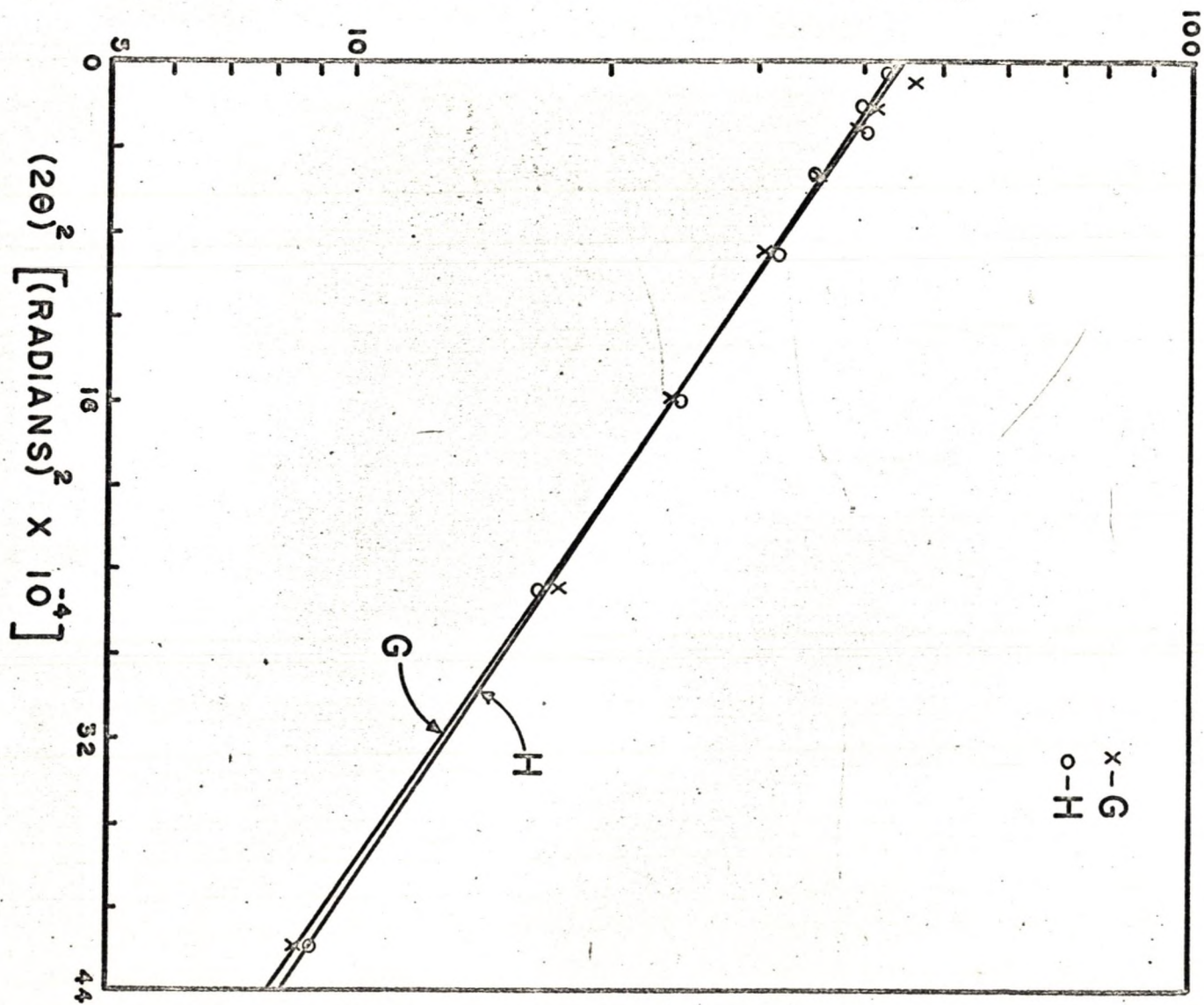


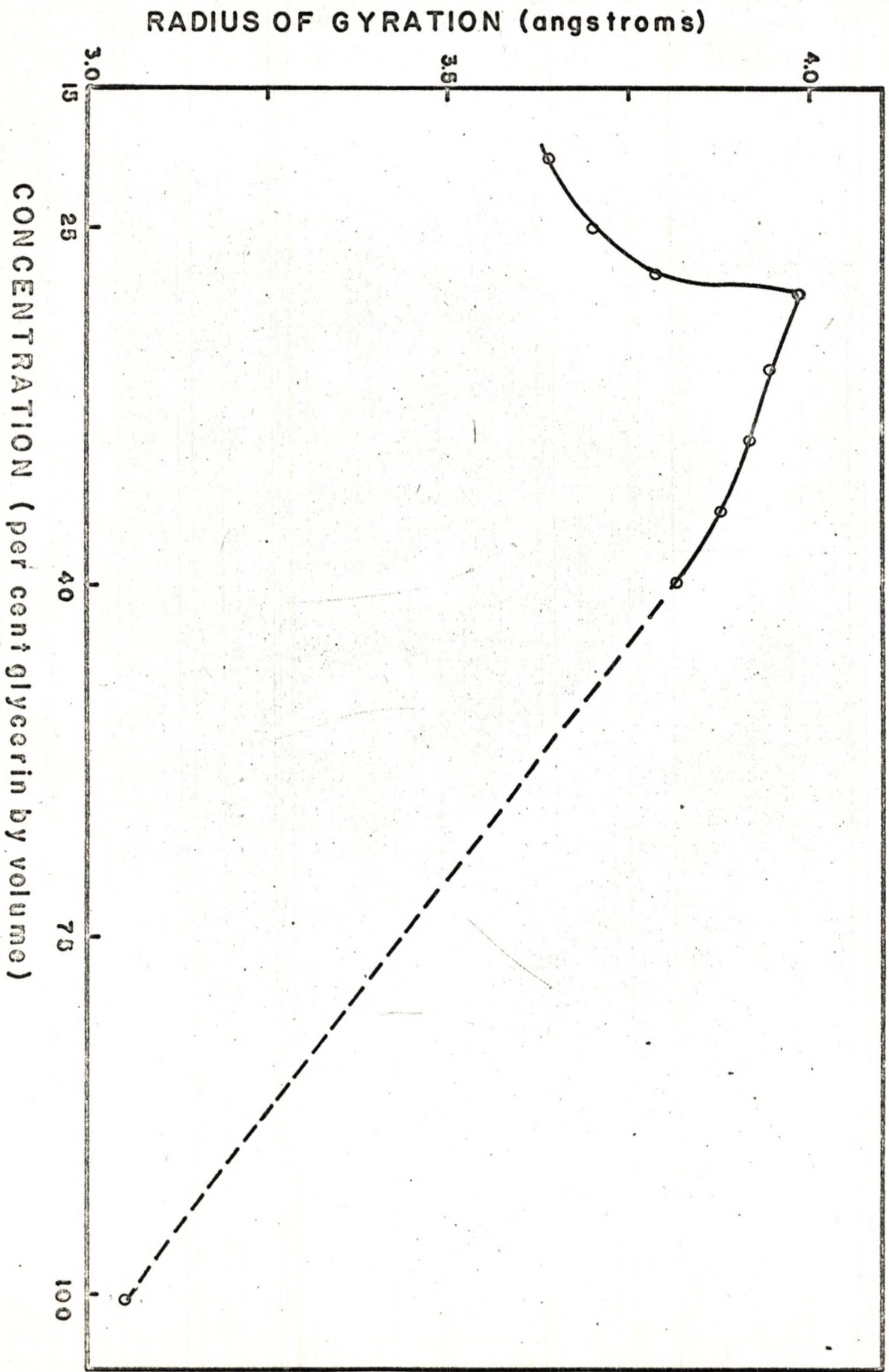
Plate VI

**Legend for Plate VI on reverse side**

Plot of the radius of gyration of ethanol-glycerin solutions as a function of concentration.

Plate VI

Plot of the radius of gyration of ethanol-glycerin solutions as a function of concentration.



IV 3000  
**Legend for Plate VII on reverse side**  
to be related

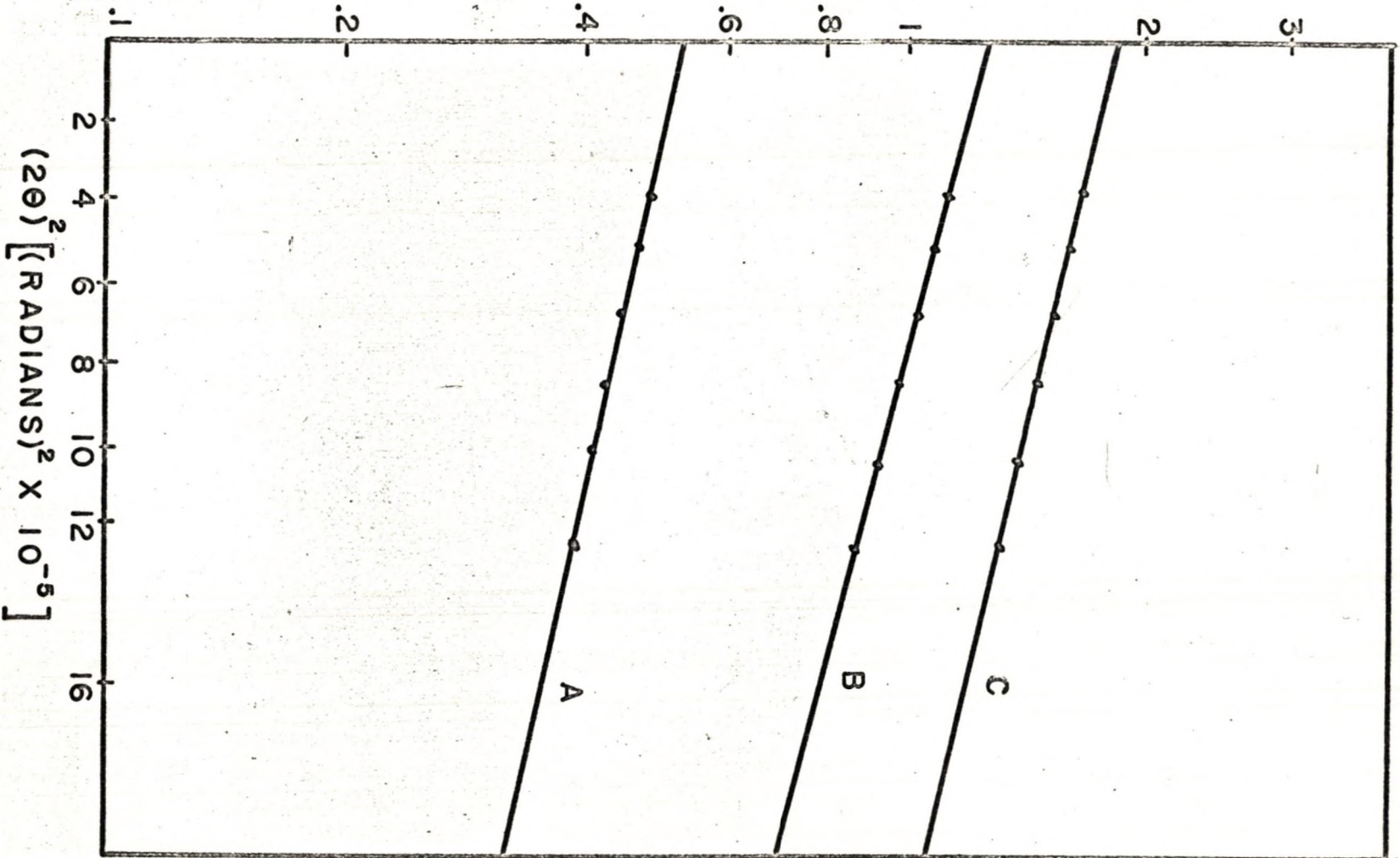


Plate VII

Guinier plot

Guinier plot of three water-tertiary butanol solutions. A,  $R_0 = 21.7$  Angstroms, Concentration = .075 mole fraction tertiary butanol; B,  $R_0 = 23.4$  Angstroms, Concentration = 0.11 mole fraction; C,  $R_0 = 21.9$  Angstroms, Concentration = 0.16 mole fraction.

(counts/sec.) CORRECTED INTENSITY



Legend for Plate VIII on reverse side

Plate VIII

abla: answer to ... mol butanol

Guinier plot

Guinier plot of three water-tertiary butanol solutions. D,  $R_0 = 21.4$  Angstroms, Concentration = 0.2 mole fraction tertiary butanol; E,  $R_0 = 20.5$  Angstroms, Concentration = 0.3 mole fraction; F,  $R_0 = 19.9$  Angstroms, Concentration = 0.4 mole fraction.

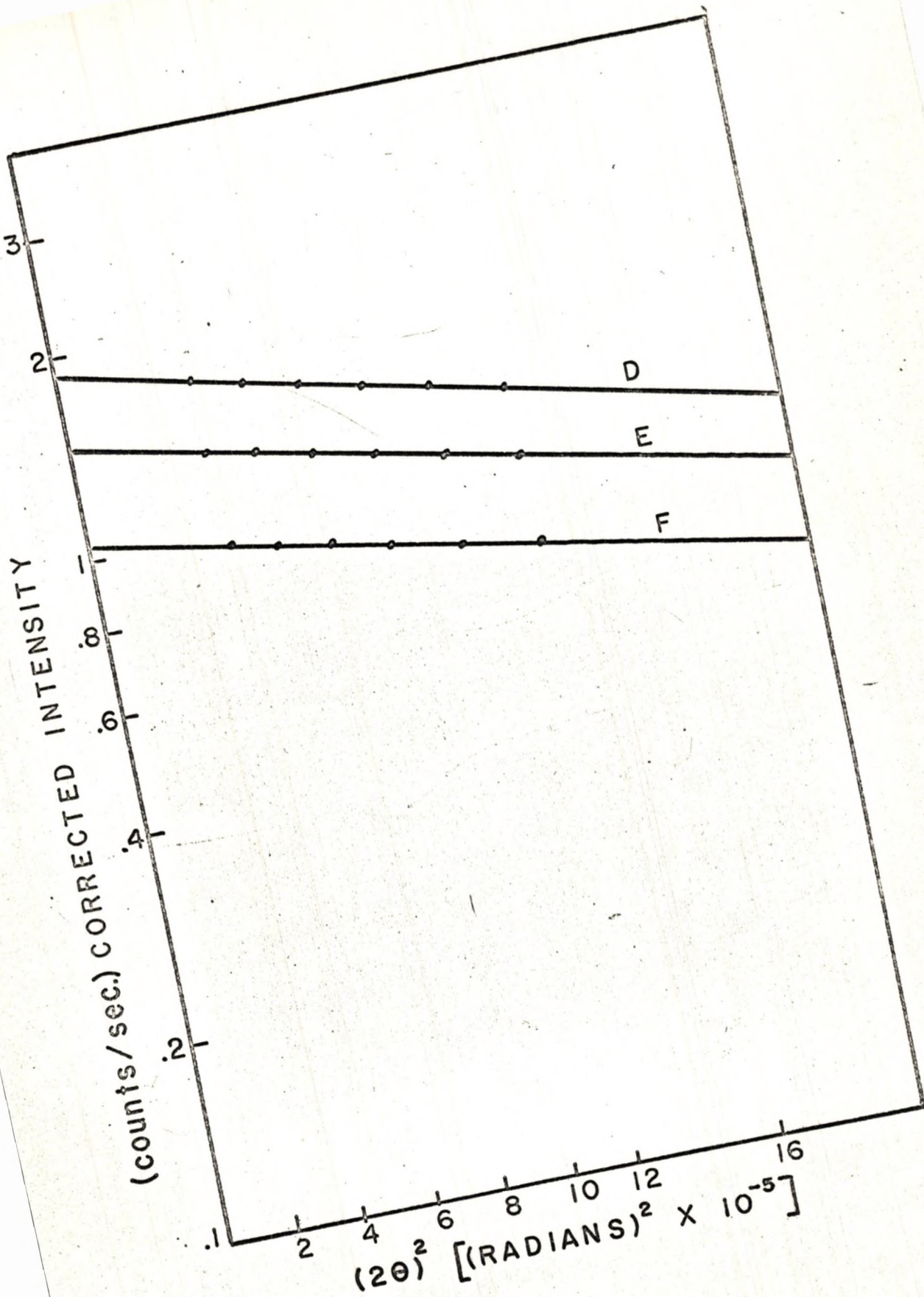


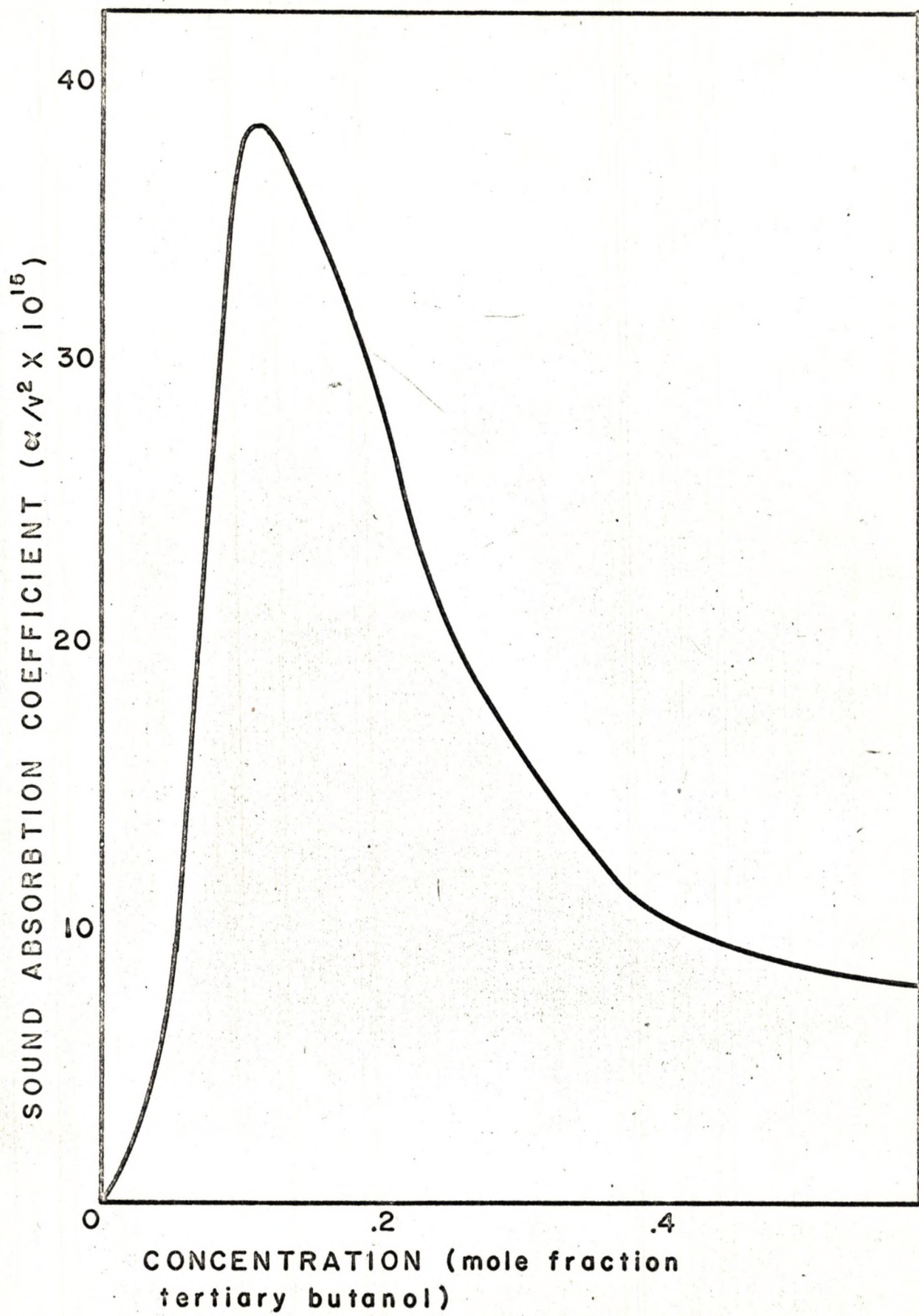
Plate IX

**Legend for Plate IX on reverse side**

Ultrasonic absorption in water-tertiary butanol  
solutions as a function of concentration.

Plate IX

Ultrasound absorption in water-tertiary butanol solutions as a function of concentration.





Legend for Plate X on reverse side  
Plot of the radius of gyration of water-soluble  
butanol solutions as a function of concentration.

Plate X

Plot of the radius of gyration of water-tertiary butanol solutions as a function of concentration.

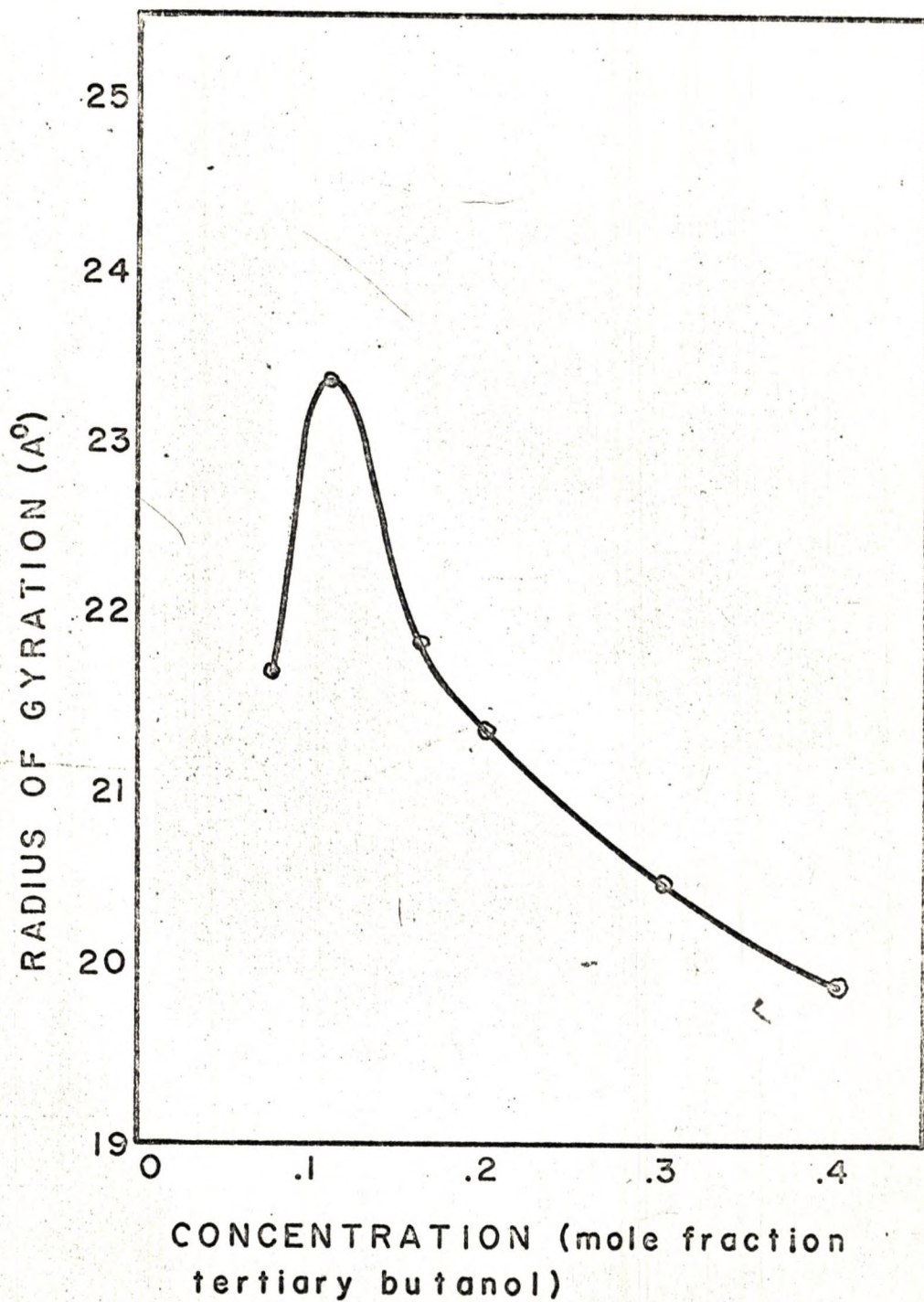


TABLE I

## TABLE OF ETHANOL - GLYCERIN SOLUTIONS

SOLUTION NO.	Concentration (per cent glycerin by volume)	Radius of Gyration (Angstroms)
A	20	3.64
B	25	3.7
C	28.5	3.79
D	30	3.99
E	35	3.95
F	40	3.93
G	45	3.88
H	50	3.82

TABLE II

## TABLE OF WATER - TERTIARY BUTANOL SOLUTIONS

SOLUTION NO.	Concentration (mole fraction tertiary butanol)	Radius of Gyration (Angstroms)	m $\alpha$ mass	$\frac{\sqrt{m}}{R_0}$
A	0.075	21.7	189	.262
B	0.11	23.4	251	.269
C	0.16	21.9	213	.272
D	0.2	21.4	165	.256
E	0.3	20.5	74	.205
F	0.4	19.9	35	.165

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