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The preparation and physical properties of benzene- and toluene-sulphonamides

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Department:

THE PREPARATION AND PHYSICAL PROPERTIES OF BENZENE- AND TOLUENE- SULPHONAMIDES.

BY

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A

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INTRODUCTION.

The formation of sulphonamide derivatives is often of distinct importance. These substances are easily purified and give sharp nepting points which make them of value for identification phases of research work. Also they are of value commercially as in the production of saccharin and other similar compounds. The purpose of this investigation is to secure information on the comparative production and yield of sulphonamides, and intermediate products, formed from their respective ring hydrocarbons, as benzene and toluene. Careful melting points are taken on purified products and solubility curves developed for different solvents. The latter give an interesting basis for comparison.

It is the hope of the author to secure later, similar data on other sulphonamide derivatives.

It is also the wish of the author to express his sincere appreciation for kindly assistance and suggestions given by Dr. W. D. Turner and Prof. H. L. Dunlap during the course of the work.

GENERAL CONSIDERATIONS.

The methods employed in synthetic production have been drawn from various sources such as are available from the publications listed in the bibliography, page 34, of this work. An effort has been made to make the methods of procedure as simple as possible.

The benzene and toluene, from which the sulphonic acids were formed, were dehydrated, purified and freshly distilled. The theoretical amount of 7 per cent fuming sulphuric acid necessary to sulphonate the quantity of benzene or toluene taken was used in each sulphonation, and the agitation and temperature controlled by means of an electrically-driven, steam-jacketed sulphonator.

The per cent yield on sulphonations was calculated from the amount of benzene or toluene actually sulphonated, thus avoiding the necessity of determining the quantity of free acid present in the sulphonates. No attempts were made at solvent extraction of the sulphonates.

A DeKhotinsky thermostat, in which constant temperature control to within one-tenth of a degree Cen-

tigrade was possible, was employed in solubility work.

In the determination of melting points of different compounds a thermometer standardized by the German Bureau of Standards was employed and full corrections made. All samples were thoroughly dried before making a determination.

PROCEDURE.

Production of Benzene Sulphonic Acid.

Benzene (3,520 grams) and 7 per cent fuming sulphuric acid (4,372 grams) were placed in a sulphonator and stirred for three hours. The acid was added in a steady stream during the first half hour. The temperature for the first hour was held at 40° C., for the second hour at 45° C., and for the third hour at 50° C. At the conclusion of the third hour the product was drawn off, allowed to stand, cool and separate into layers. The layers were then separated. There was found to be 5231 grams of benzene sulphonic acid, 1309 grams of sulphuric acid and 1144 grams of benzene present. A loss of 3 per cent occurred due to evaporation and mechanical manipulation. The actual yield was 68 per cent of the theoretical.

A similar synthesis gave a yield of 66 per cent and a loss of 3 per cent.

Production of Ortho- and Para-toluene Sulphonic Acids.

Toluene (3,480 grams) and 7 per cent fuming sulphuric acid (3,552 grams) were placed in a sulphonator and stirred at a temperature of 75-80° C., for three hours. The acid was added in a steady stream during the first half hour. After the three hours had elapsed the products were drawn from the sulphonator, allowed to stand, and cool and separate into layers. The lower layer of sulphonate was dark brown in color and very viscous at 20° C. There was found to be 6542 grams of ortho- and para-toluene sulphonic acid, 355 grams of sulphuric acid, and 322 grams of toluene present. There was a loss of three per cent due to evaporation and mechanical manipulation. The actual yield was 90 per cent of the theoretical. (See General Conclusions, page J1, with regard to this yield.

Formation of the Sodium Salt of Benzene Sulphonic Acid.

An excess of saturated sodium chloride solution was added to the sulphonic acid and the mixture stirred thoroughly and permitted to stand. No crystal formation was evident. A small quantity of the liquid showed no crystals after standing at room temperature for two weeks. Accordingly the entire mixture was placed in a large porcelain evaporating dish and concentrated till a test showed crystal formation upon cooling. The whole solution was then cooled, the crystals of sodium benzene sulphonate filtered off, centrifuged, and dried. The liquor obtained from centrifuging was added to the filtrate. This process was continued till only a small amount of mother liquor remained. The dried sodium benzene sulphonate was recrystallized from absolute alcohol in order to remove any sodium chloride, sodium sulphate, or other impurity present. This was accomplished by placing a quantity of impure crystals in a round-bottom flask, adding absolute alcohol, heating the alcohol to its boiling point, and filtering by suction through a filter paper in a glass funnel containing a porcelain cone. The filtrate was chilled and the crystals formed were filtered off, centrifuged, and dried. These dried crystals were again put into solu-

tion in hot absolute alcohol, the solution filtered and cooled, and the resulting crystals filtered off, centrifuged and dried. A pure product of sodiumbenzenesulphonate was thus obtained. Tests were made to determine the complete absence from the crystals of such impurities as sodium chloride and sodium sulphate. A yield of approximately 81 per cent was secured. A part of the 19 per cent loss was due to mechanical manipulation, unsulphonated benzene present in the sulphonate, (See General Conclusions, page 31.), and to the final bit of mother liquor that was not brought to dryness and the crystals purified.

Extractions were run on each crystallization of the sodium salt from the mother liquor. A weighed amount of the dried sodium salt was placed in an extraction thimble and extracted 3 hours with absolute alcohol. The loss in weight at the conclusion of the extraction gave the amount of pure sodiumsulphobenzoate present as the insoluble sodium chloride, sodium sulphate and other impurities remained in the thimble. The extraction solution of alcohol was evaporated to dryness and a check run on the amount of sodiumbenzenesulphonate present. The sodiumbenzenesulphonate obtained from the extraction solution was also tested to determine if any sodium chlor-

ide, sodium sulphate or other impurities were present. It was found that the extraction gave only pure sodium-benzenesulphonate. The crystals of sodium salt were thoroughly dried before the extraction was started in order to remove all water present, especially from the sodium sulphate. Sodium sulphate containing water of crystallization is somewhat soluble in absolute alcohol. A curve, page 19, was plotted with the per cent of impurity present in the product of each crystallization against the serial number of the crystallization. The only variable was that no definite per cent of water was volatilized before each cooling to crystal formation. The crystallization was governed by frequent testing of small portions of the mother liquor to find if crystals separated upon cooling.

Formation of the Sodium Salt of Ortho- and Para-Toluene Sulphonic Acids.

The mixture of ortho- and para-toluene sulphonic acids and free sulphuric acid was treated with an excess of a saturated solution of sodium chloride. After standing for a period of 18 hours a slight formation of crystals was noticeable. The mixture was now placed in a large porcelain evaporating dish and fractionally crystallized till only a small amount of mother liquor remained. The crystallization product of ortho- and para-sodiumsulphotoluate was purified and tested in the same manner as described under "Formation of the Sodium Salt of Benzene Sulphonic Acid", page 8, A yield of approximately 77 per cent was secured and some loss was due to mechanical manipulation, unsulphonated toluene present in the sulphonate, (See General Conclusions, page 31.), and unused mother liquor. A curve was plotted, page 20, with the per cent impurities against the serial number of the crystallization, similar to the one plotted for the crystallizations of the sodiumsulphobenzoate, page 19, and subject to the same variable.

Conversion of Sodiumsulphobenzoate to Benzenesulphonchloride.

A quantity of sodiumbenzenesulphonate was placed in a porcelain evaporating dish, treated with an excess of phosphorus pentachloride and warmed on a water-bath till the action was complete. This reaction should be carried on in a hood and care taken to avoid inhaling the fumes or permitting them to attack the eyes. Cold water was now slowly added and the liquid contents of the evaporating dish transferred to a suitable separatory funnel. The lower oily layer of benzenesulphonchloride was drawn off and washed several times with water. The specific gravity was found to be 1.385. A yield of 76 per cent of the theoretical was secured. Three duplicate conversions gave yields of 79, 76, and 75 per cent of the theoretical.

Conversion of Ortho- and Para-sodiumsulphontoluate to Ortho- and Para-toluenesulphonchloride.

A quantity of ortho- and para-sodiumsulphotoluate was treated with an excess of phosphorus pentachloride, warmed and set in a hood till the reaction was complete. Cold water was slowly added and the solid paratoluenesulphonchloride filtered from the water and liquid orthotoluenesulphonchloride by suction. The para compound was washed with water, centrifuged to remove the last traces of orthotoluenesulphonchloride, again washed with water, and then dried by vacuum. The melting point of the product of paratoluenesulphonchloride was found to be 69.3°C. A yield of 79 per cent of the theoretical was secured. A duplicate synthesis gave a yield of 78 per cent of the theoretical.

Synthesis of Benzenesulphonchloride to Benzenesulphonamide.

To a quantity of benzenesulphonchloride a slight excess of concentrated ammonia was added over the amount theoretically required to complete the reaction. Upon completion of the reaction the resulting clear solution was boiled till only a slight test for ammonia gas could be detected in the vapors. The solution was now chilled, the crystals of benzenesulphonamide filtered off, washed with a small amount of water, and dried. These crystals were in turn recrystallized from concentrated ammonia and from alcohol before they were considered of sufficient purity for solubility work. The melting point of the final benzenesulphonamide was found to be 151.1° C. A yield of 81 per cent of the theoretical was secured. A duplicate synthesis gave a yield of 82 per cent.

Synthesis of Paratoluenesulphonchloride to Paratoluenesulphonamide.

A quantity of paratoluenesulphonchloride was treated with concentrated ammonia till the conversion to the amide was complete. The resulting clear solution was boiled till only a slight excess of ammonia remained and then the solution was cooled, and the crystals purified in the same manner as described for benzenesulphonamide crystals under Synthesis of Benzenesulphonchloride to Benzenesulphonamide on page 14. The final product of paratoluenesulphonamide gave a melting point of 137.7° C. A yield of 71 per cent of the theoretical was secured. A duplicate synthesis gave a yield of 75 per cent.

SOLUBILITIES.

Solvents and Solutes.

The solvents used were alsolute alcohol and pure water. The alcohol was made absolute by distillation from lime followed by a second distillation from anhydrous copper sulphate and by a final standing over metallic calcium. The water was freshly distilled and tested for purity.

The compounds whose solubilities were determined were those prepared by methods outlined under "Procedure", page 6.

Solubilities were determined at 15, 30, 45, and 60°C. All compounds were thoroughly dried before starting a determination.

Method for Determination of Solubilities.

Solute and solvent were placed in 250 c.c. glass bottles fitted with ground-glass stoppers, heated to the degree of temperature at which they were to be subjected, and the stoppers tightly fastened. This preheating served to counteract subsequent pressure which might be developed and as a guide to the approximate propor-

tions of solute to solvent. The bottles were tested for leakage, placed in a constant-temperature DeKhotinsky thermostat, and rotated continuously for 10 hours. At the conclusion of this 10 hour rotation the bottles were removed from the rotator and, after loosening the stoppers, left standing in the thermostat for a short time to permit the solute to settle. With pipettes, heated in an electric oven to a temperature slightly higher than the temperature of the thermostat, a small amount of the solvent containing the solute in solution was placed in tared, glass-stoppered weighing bottles. The reason for the use of heated pipettes was to prevent the crystallization of the solute from the warm solvent. The weighing bottles were cooled in a desicator, weighed, transferred to the electric oven, and the solvent evaporated at about 10°C., below its boiling point. After complete drying the weighing bottles and contents were cooled in a desicator, weighed, and the grams solute in 100 grams solvent calculated. These calculations were not taken for final in curve plotting till they were checked in triplicate to the second decimal place from different determinations. The amount of solvent containing solute in solution that was placed in the tared weighing bottles depended upon the solubility of the solute. The greater the solubility of the solute

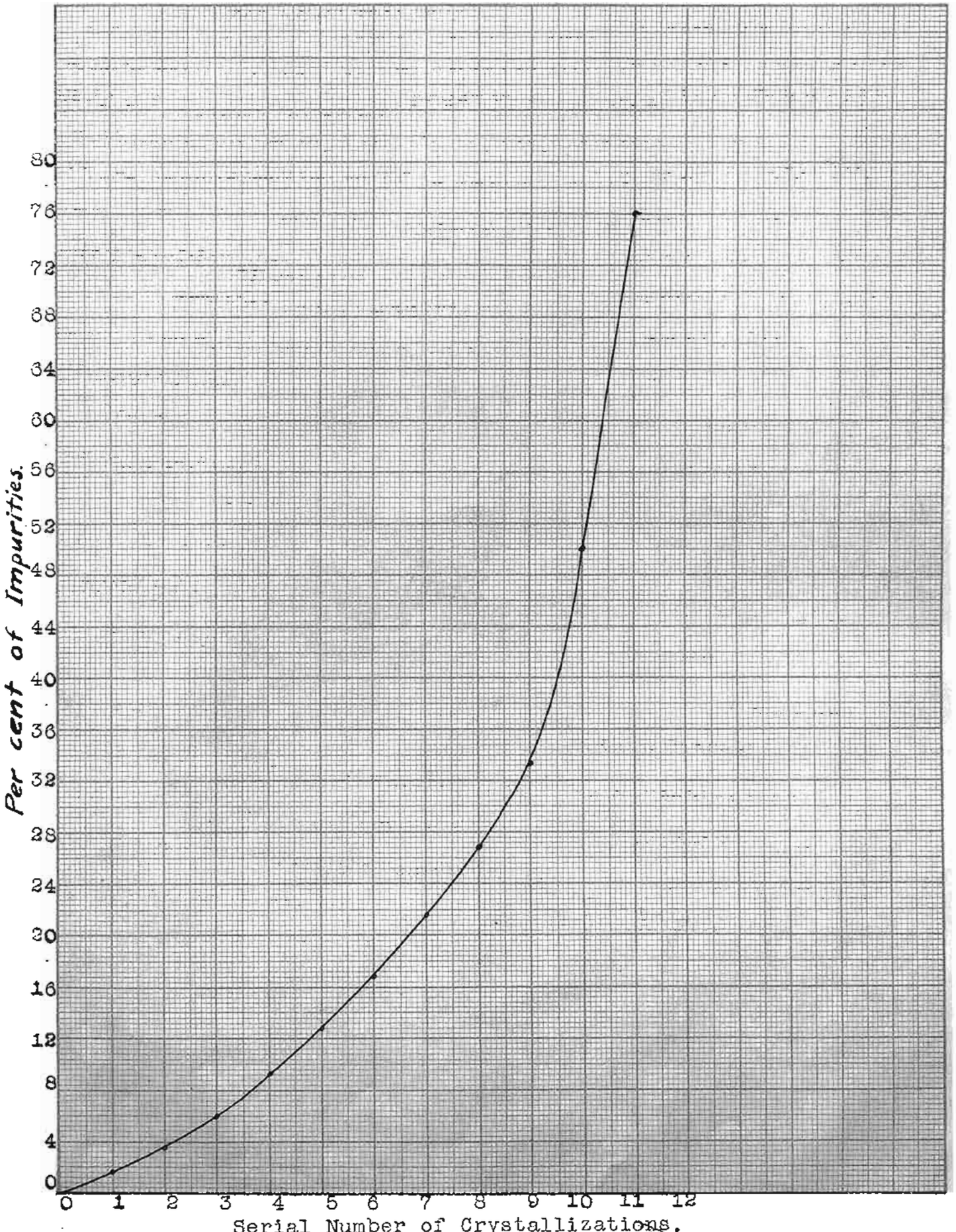
the more difficult it was to obtain a thorough evaporation and drying. The pipettes were inverted to permit of faster transference of liquid and a short piece of rubber tubing attached to prevent burning the lips.

Curves.

Curves were plotted which show the solubility of sodiumbenzenesulphonate, ortho- and para-toluenesulphonate, benzenesulphonamide and paratoluenesulphonamide in pure water and absolute water at various temperatures. Two sheets of comparative curves were also drawn. A complete list of these curves can be found in the index, page 39.

MISSOURI SCHOOL OF MINES

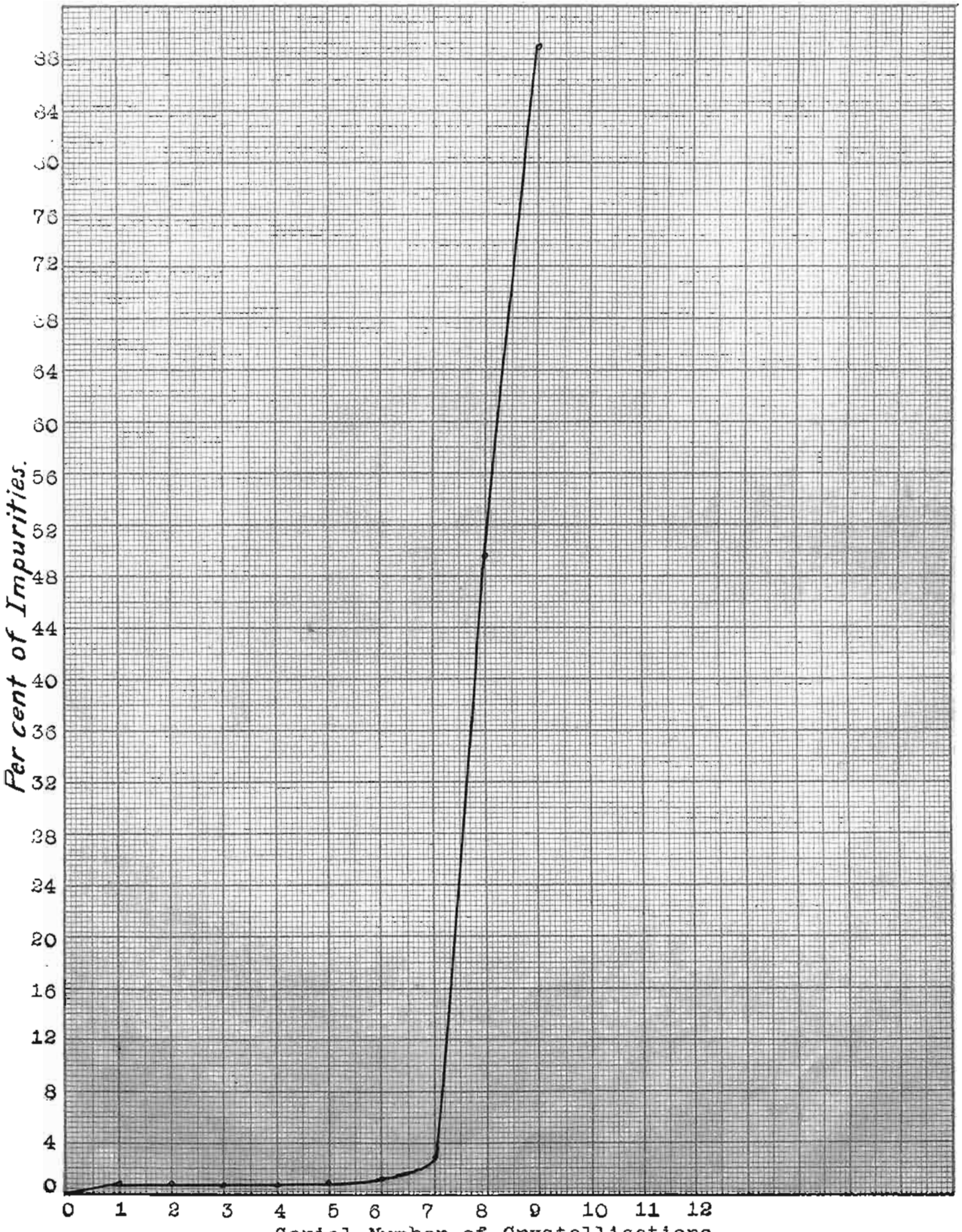
Crystallization of Sodiumsulphobenzoate.



Form E—5m—9-17—B.P.Co.

MISSOURI SCHOOL OF MINES

Crystallization of Ortho- and Para-Sodiumsulpho-Toluate.



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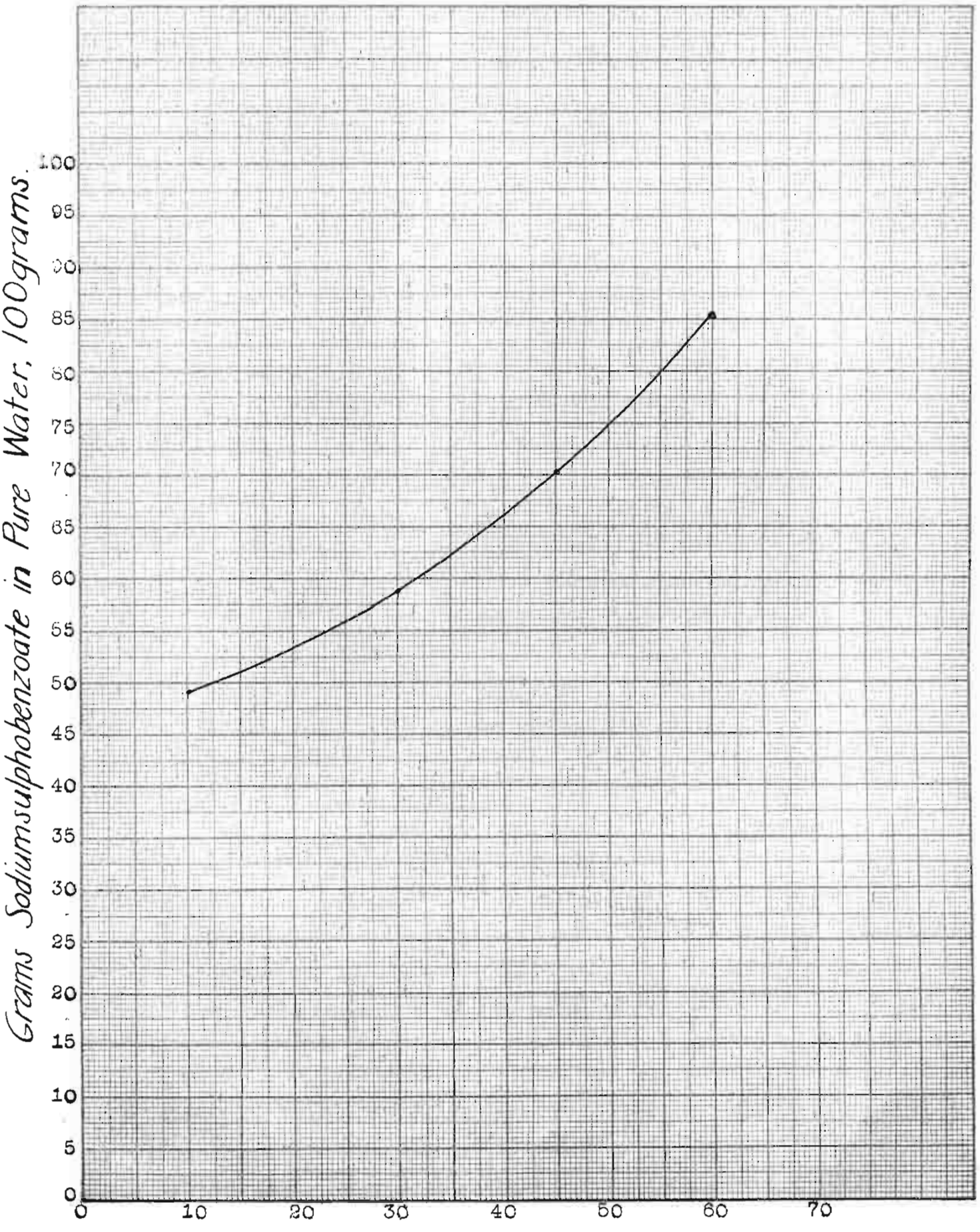
Solubility Curve for Sodiumsulphobenzoate in Pure Water.



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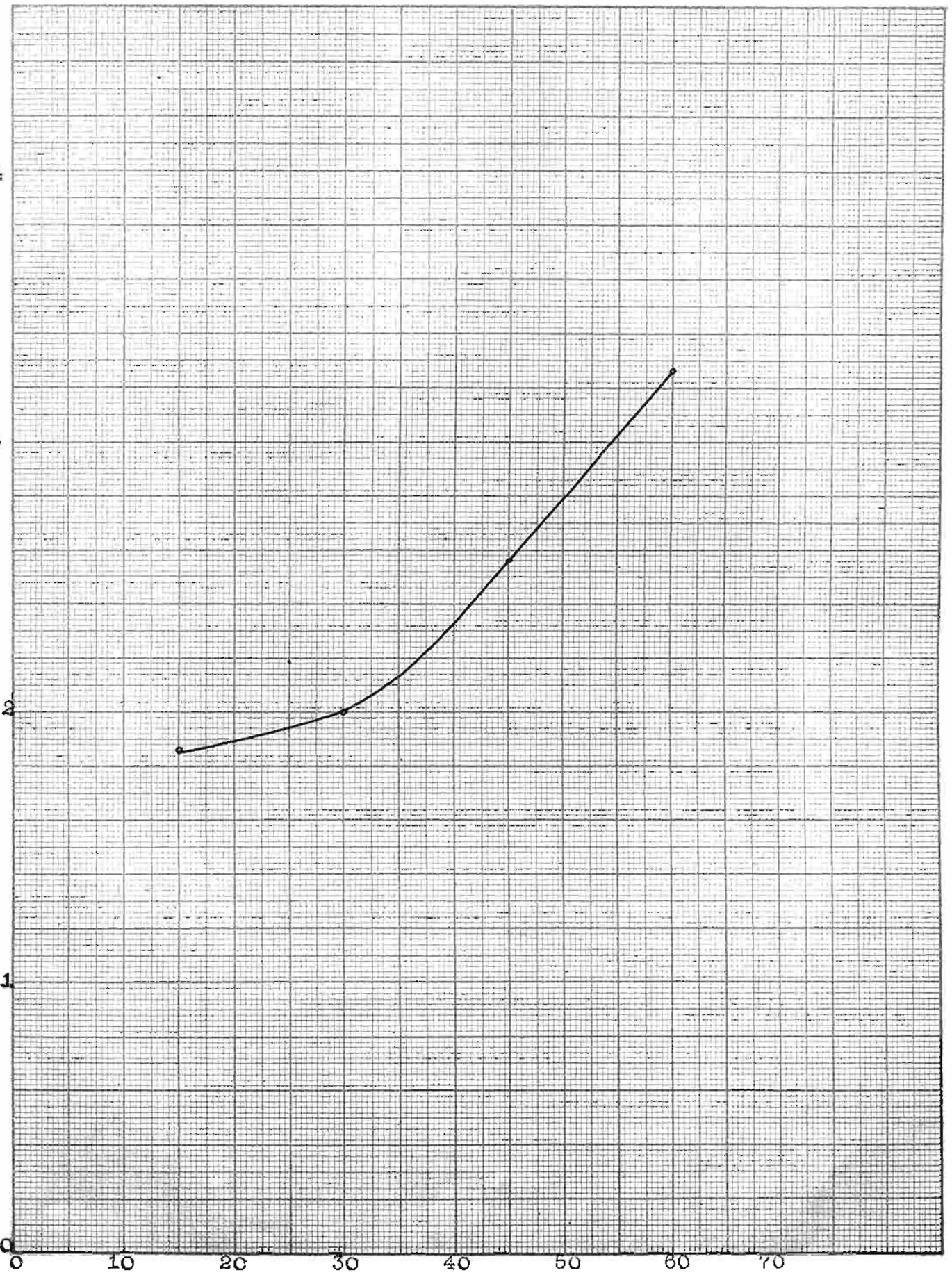
Solubility Curve for Sodiumsulphobenzoate in Absolute Alcohol.



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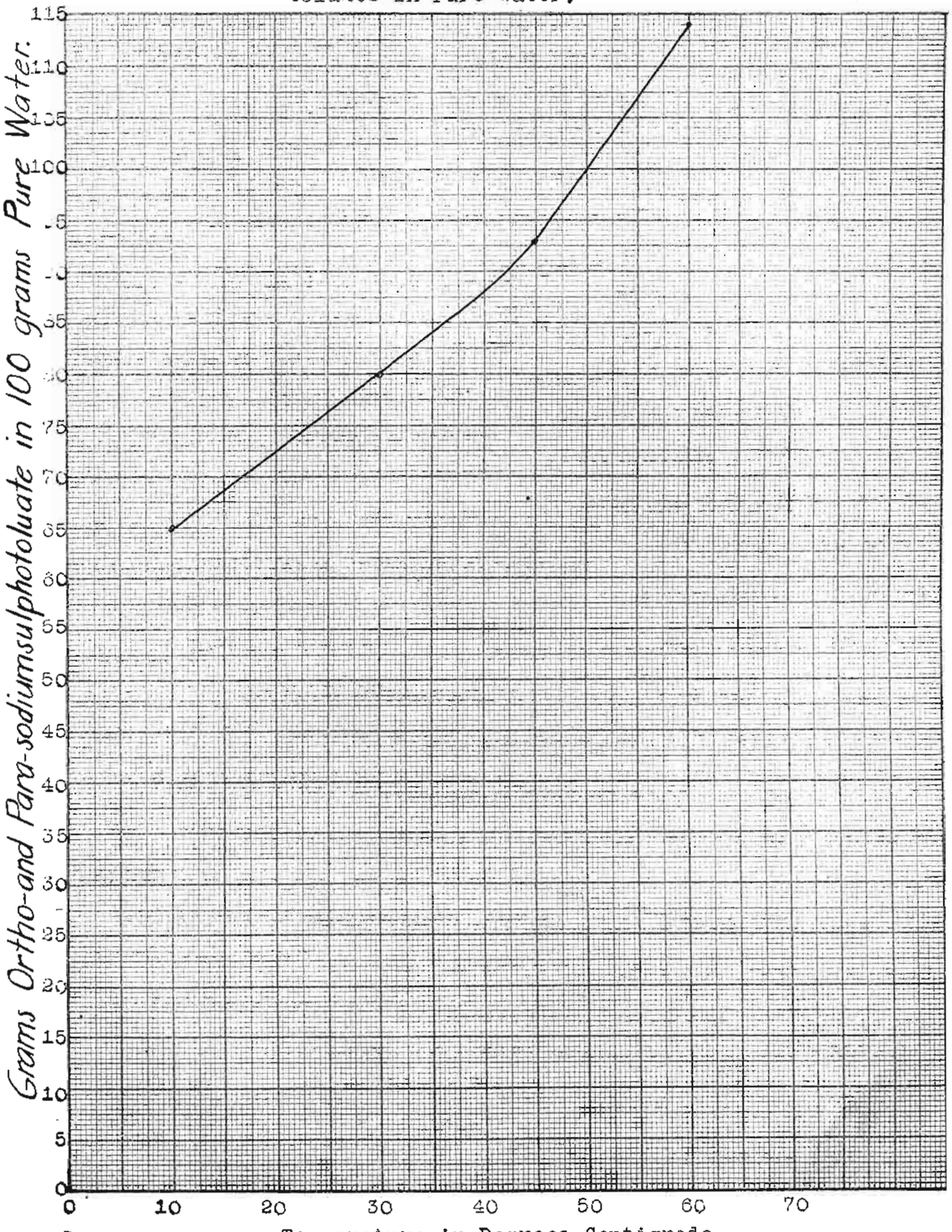
Solubility Curve for Ortho- and Para-sodiumsulpho-toluate in Pure Water.



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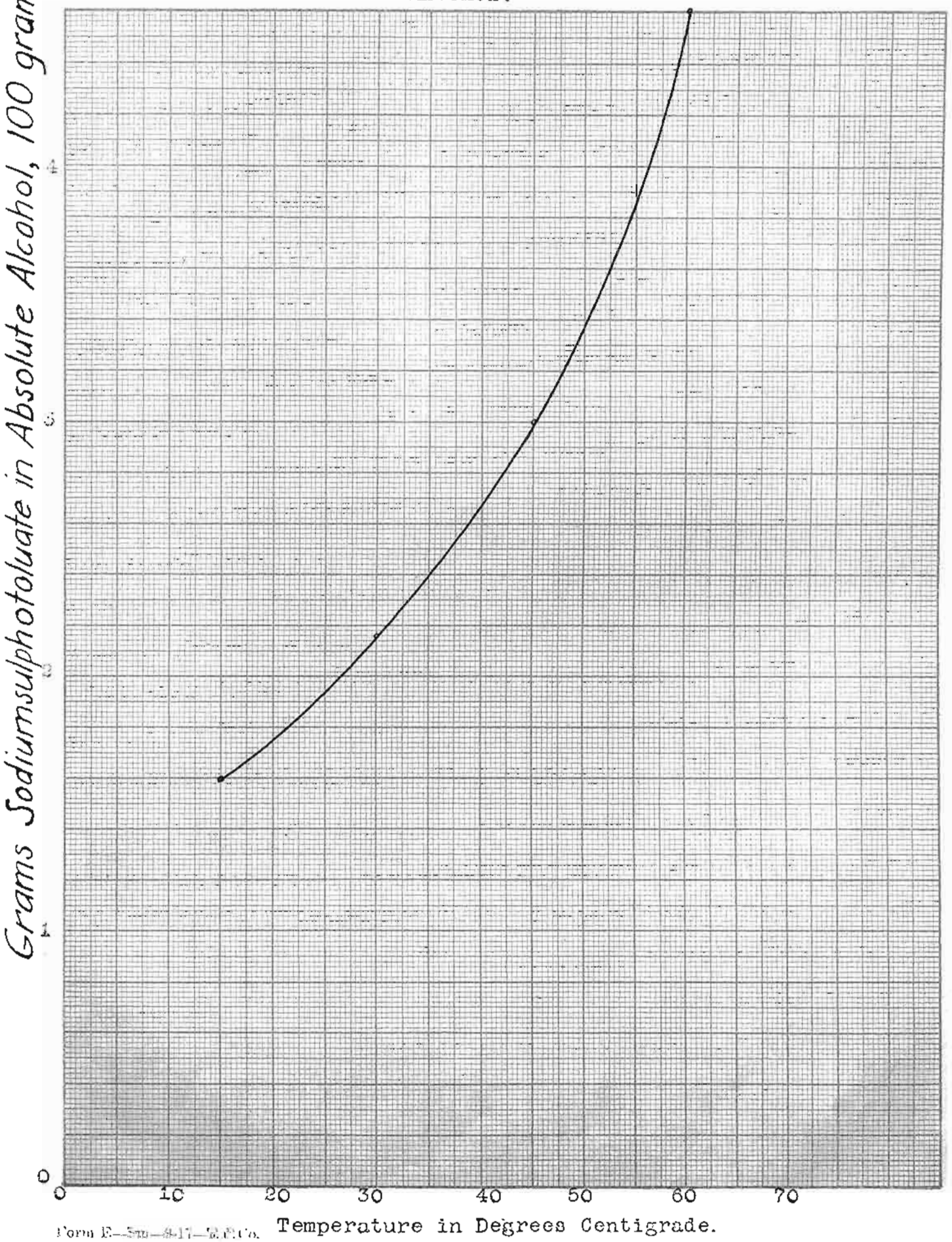
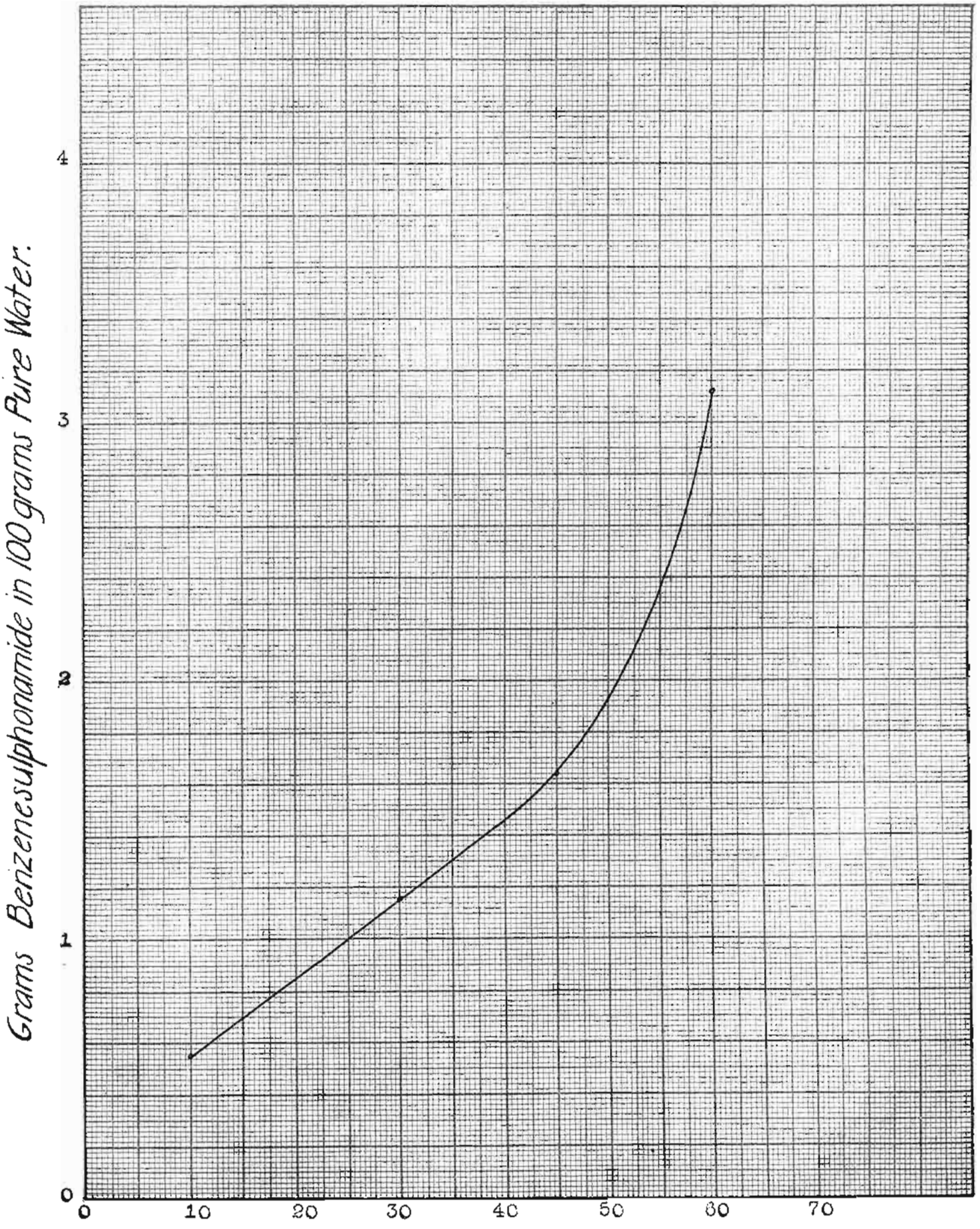
Solubility Curve for Sodiumsulphotoluate in Absolute Alcohol.



MISSOURI SCHOOL OF MINES

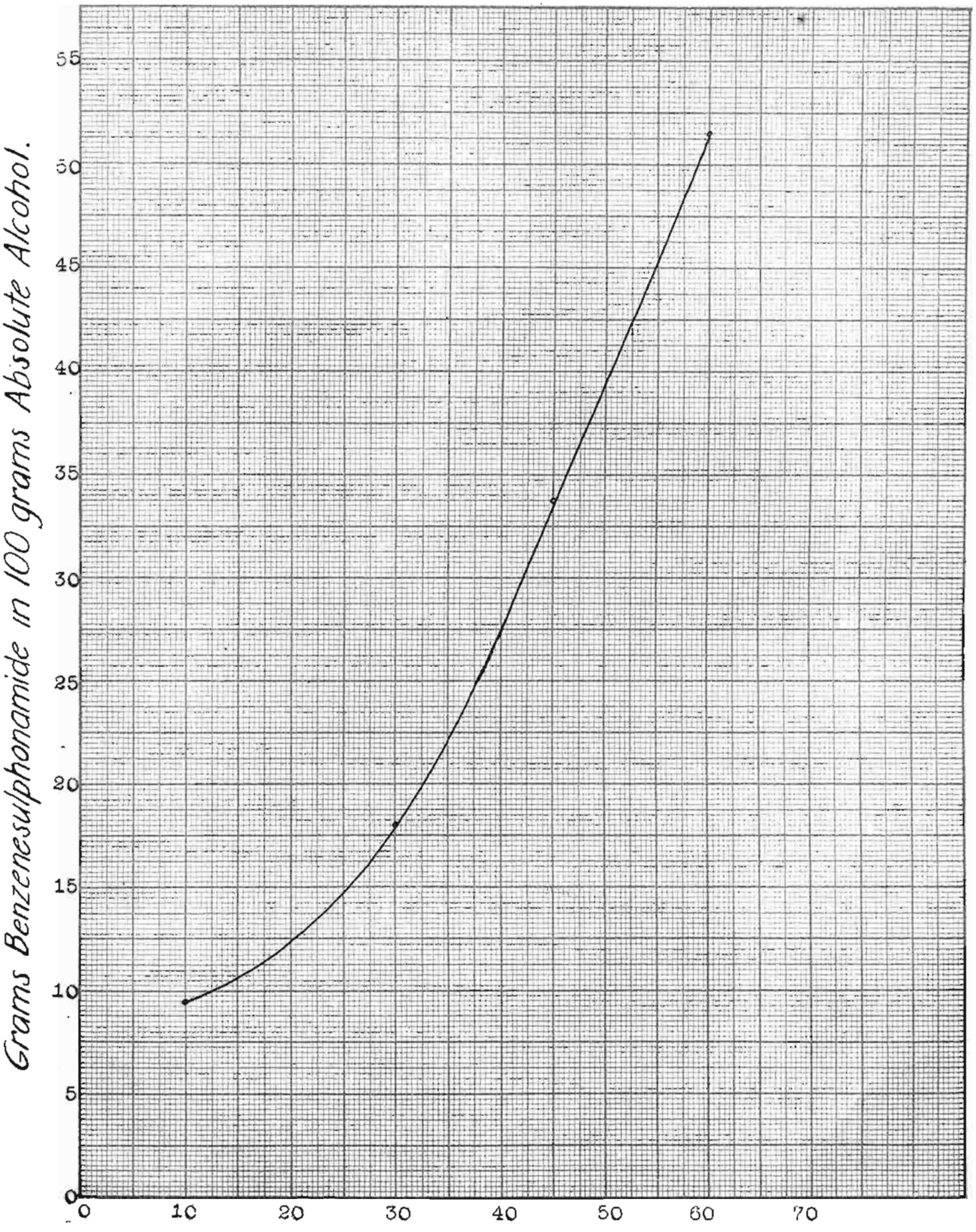
Solubility Curve for Benzenesulphonamide in Pure Water.



Form E—5m—9-17—R. P. Co.

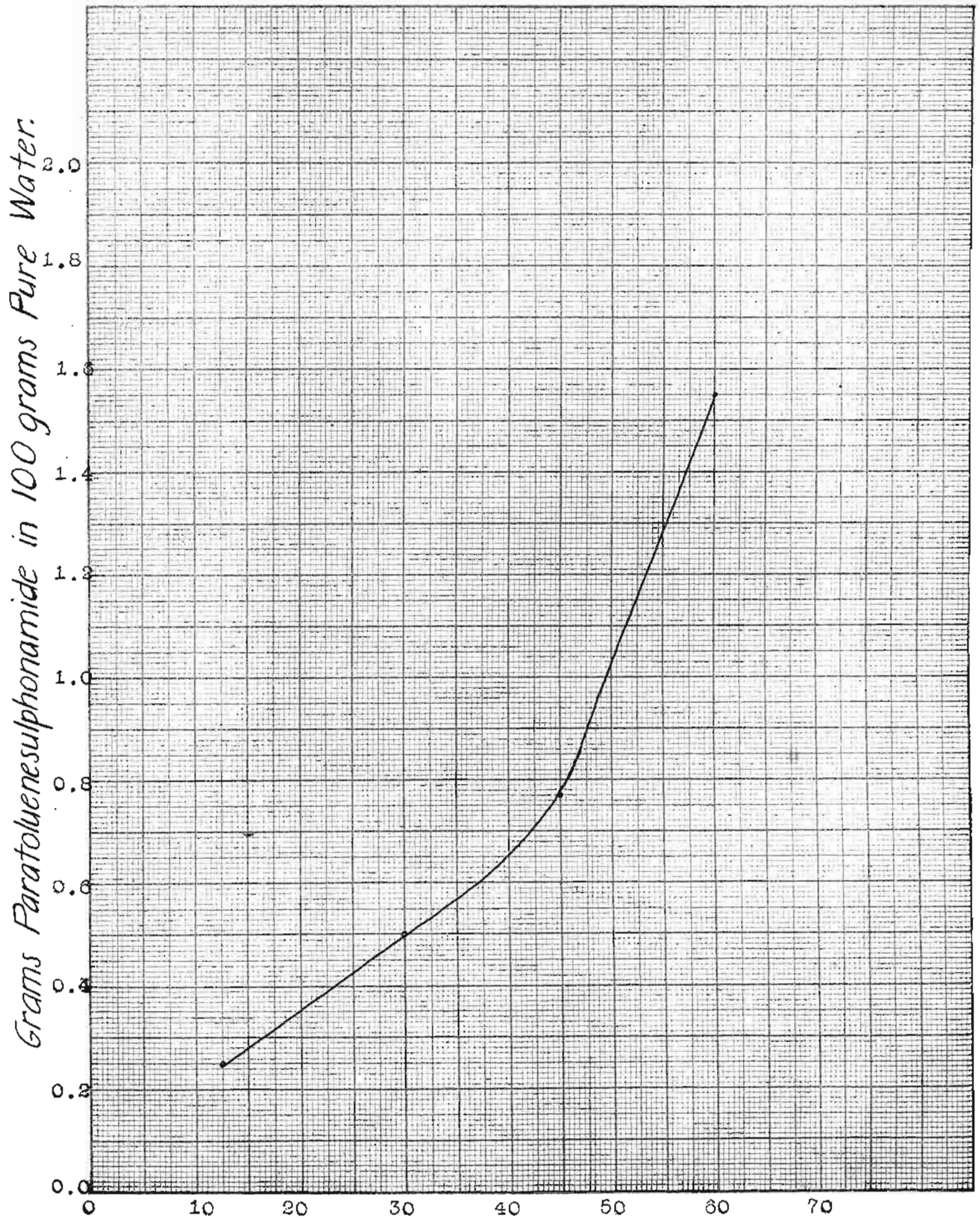
MISSOURI SCHOOL OF MINES

Solubility Curve for Benzenesulphonamide in Absolute Alcohol.



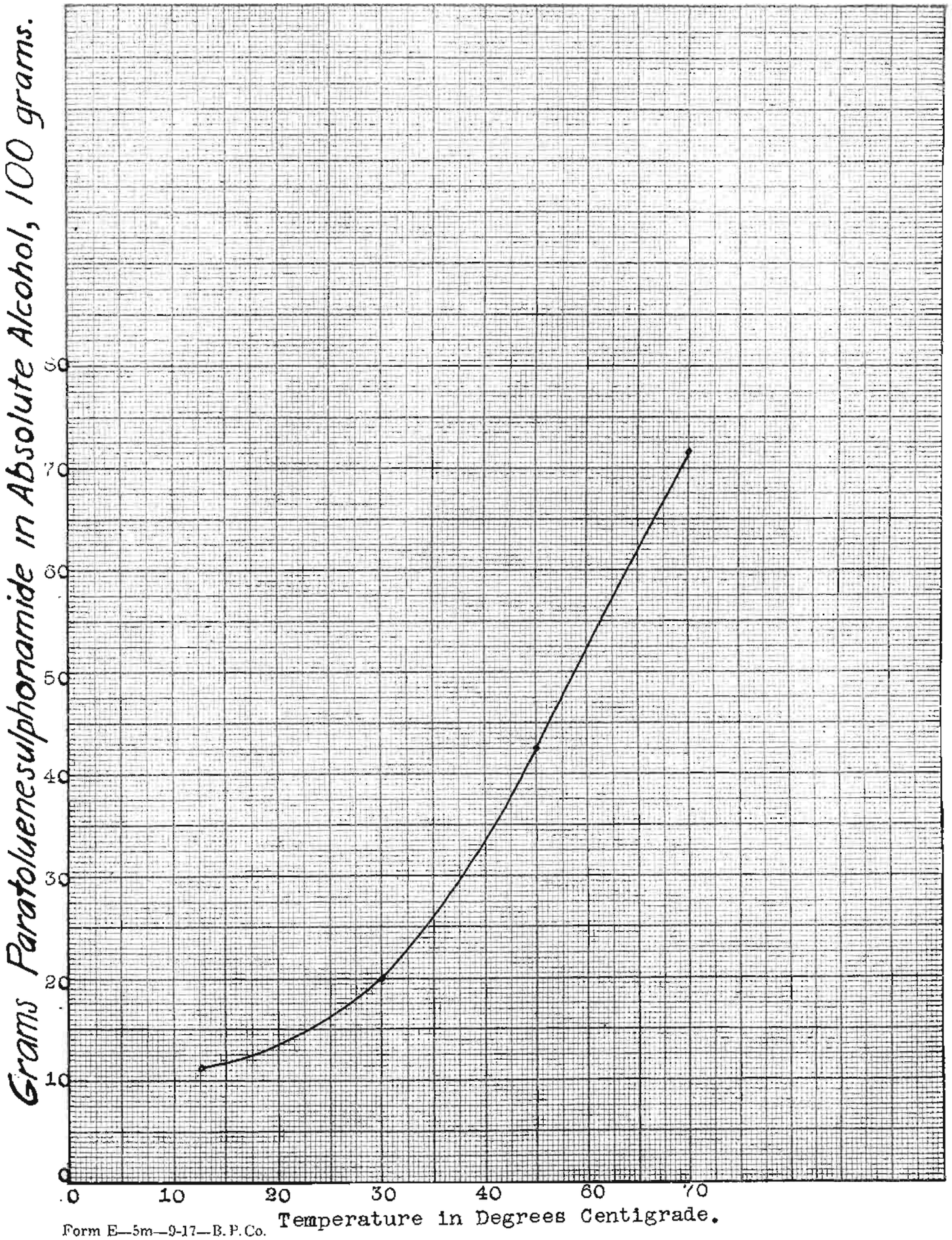
MISSOURI SCHOOL OF MINES

Solubility Curve for Paratoluenesulphonamide in Pure Water.



MISSOURI SCHOOL OF MINES

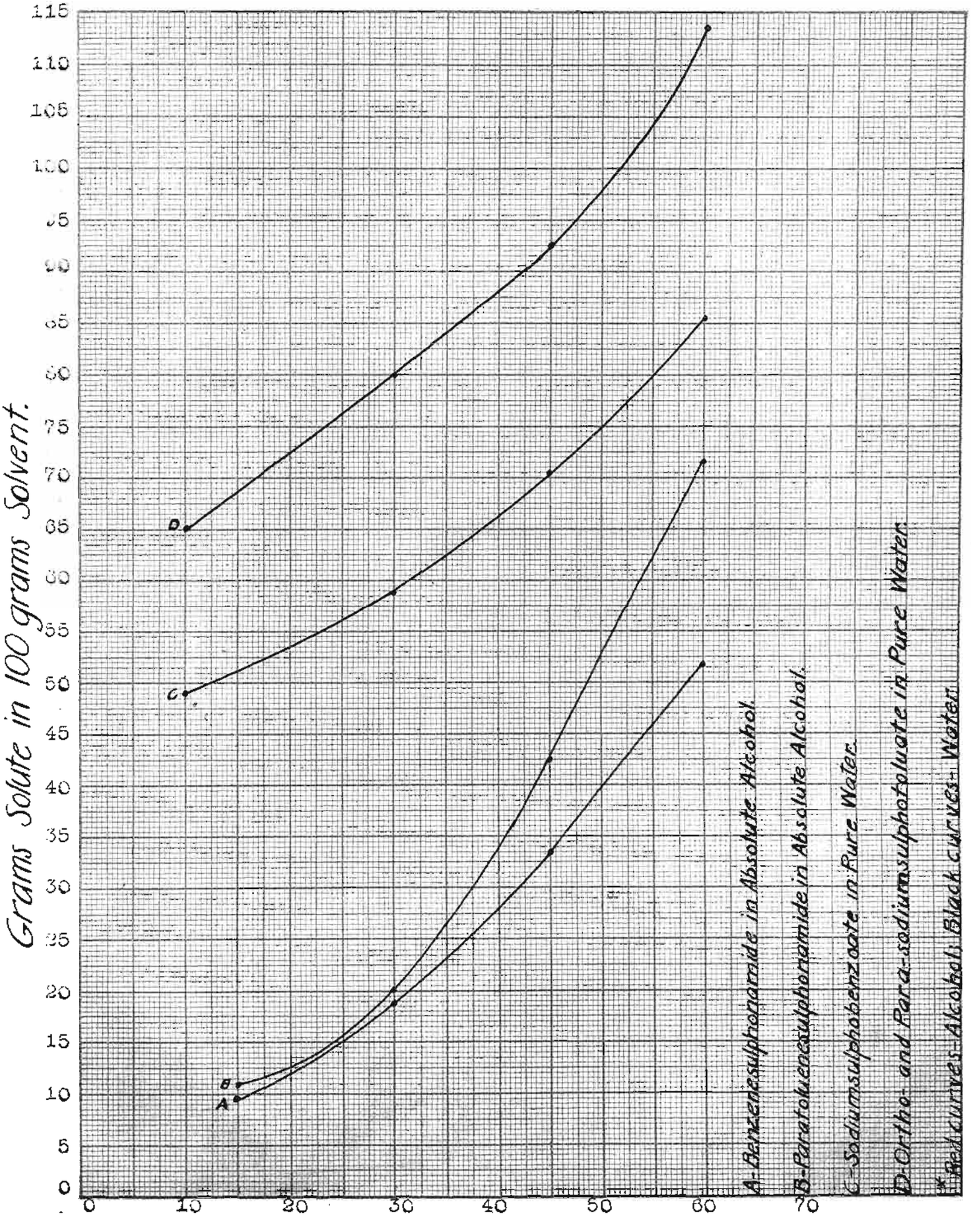
Solubility Curve for Paratoluenesulphonamide in Absolute Alcohol.



Form E—5m—9-17—B. P. Co.

MISSOURI SCHOOL OF MINES

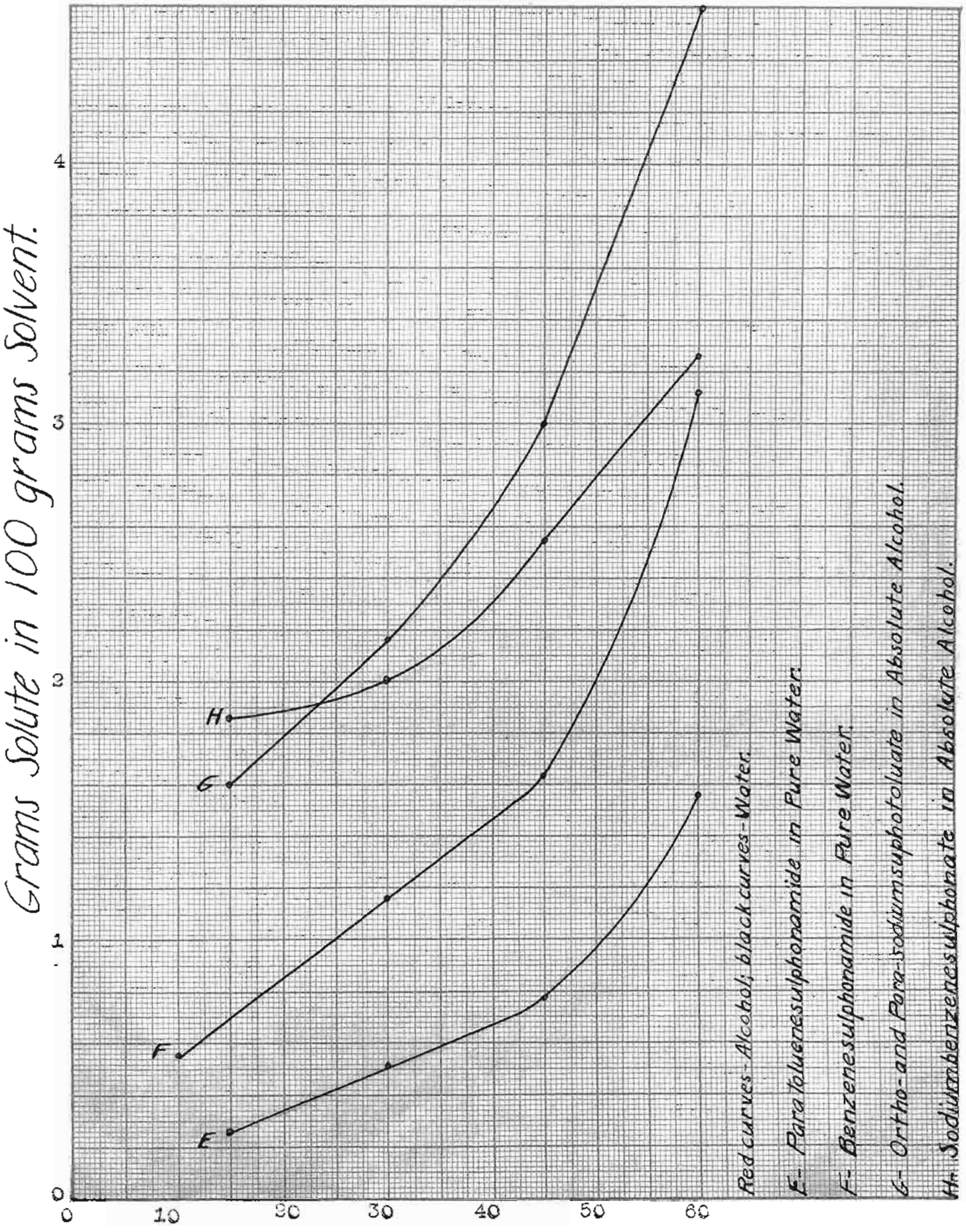
Comparison of Solubility Curves.



Form E—3m—9-17—B.P.Co. Temperature in Degrees Centigrade.

MISSOURI SCHOOL OF MINES

Comparison of Solubility Curves.



Temperature in Degrees Centigrade.

GENERAL CONCLUSIONS.

Benzene sulphonated with the theoretical amount of 7 per cent fuming sulphuric acid and agitated for 3 hours at a temperature of 40-50°C., gave a yield of 67 per cent of the theoretical and a loss of 3 per cent due to evaporation and mechanical manipulation.

Toluene sulphonated with the theoretical amount of 7 per cent fuming sulphuric acid and agitated for 3 hours at a temperature of 75-80°C., gave a yield of 90 per cent of the theoretical and a loss of 3 per cent due to evaporation and mechanical manipulation. However it is very probable that this 90 per cent yield is too high since some of the toluene must have been contained in the viscous sulphonate. (See "General Considerations", page 4, as to the calculation of yields.) It would be necessary to extract the sulphonic acids to get quantitative data on the amount of benzene or toluene present.

A comparison of the two curves, page 19-20, show the ortho- and para-sodiumtoluenesulphonate is more insoluble in a hot, acid solution of its mother liquor than the sodiumbenzenesulphonate under similar conditions. The bulk of the former comes off in the

first 7 crystallizations with less than 4 per cent of impurity, while the latter largely comes off in the first 9 crystallizations with slightly more than 27 per cent of impurity.

The chlorination of sodiumbenzenesulphonate gave a yield of 77 per cent of the theoretical for benzenesulphonchloride.

The chlorination of ortho- and para-sodiumtoluenesulphonate gave a yield of 79 per cent of the theoretical for the chloro-derivative. This was entirely paratoluenesulphonchloride for the ortho isomer was discarded at this point. The ortho isomer was of only slight amount.

In the formation of benzenesulphonamide and paratoluenesulphonamide from benzenesulphonchloride and paratoluenesulphonchloride the yield was 81 per cent and 73 per cent respectively of the theoretical yield.

The melting points of pure compounds were found to be:

Paratoluenesulphonchloride-------69.3° C.
Benzenesulphonamide-------------151.1° C.
Paratoluenesulphonamide---------137.7° C.

The specific gravity of benzenesulphonchloride was found to be 1.385 at 20° C.

Sodiumsulphobenzoate and ortho- and para-sodiumtoluenesulphonate were more soluble in pure water than their corresponding sulphonamide derivatives. Ben-

zenesulphonamide and paratoluenesulphonamide were more soluble in absolute alcohol than the sodium salts of benzene- and toluene-sulphonic acids. Ortho- and para-sodiumtoluenesulphonate was more soluble in pure water and absolute alcohol than was sodium benzenesulphonate. However below 25° C., the reverse was true but above the temperature of 25° C., the general statement holds true. Benzenesulphonamide was more soluble in pure water than paratoluenesulphonamide but in absolute alcohol the para-toluenesulphonamide was the more soluble.

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