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HYDROTROPIC SOLVENTS FOR BENZOIC ACID:
PHASE EQUILIBRIA

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TABLE OF CONTENTS

ABSTRACT

Hydrotropic solutions are aqueous salt solutions which effect increased solubility of substances insoluble or slightly soluble in water at the same temperature. It is a "salting-in" effect as compared with the more commonly known "salting-out" effect. Relatively concentrated salt solutions are required to effect a marked change in solubility of the third component. In general, the third component is reprecipitated by diluting with two to three volumes of water. The solvent may then be made ready for re-use by reconcentration by evaporation.

Commercial applications for these solvents are found in extraction processes, electrochemical reactions, organic reactions and as crystallization media. They have advantages over organic solvents in that they are non-volatile, non-flammable, good conductors of electricity, may be used at any pH, and others.

There have been many investigations as to the types of salts that act as hydrotropes and the types of substances dissolved. Solubility data for several systems has been published, but no complete phase equilibria data has been determined.

The purpose of this investigation was to determine phase equilibria data at 30°, 40°, and 60°C. for the system, water, sodium o-xylenesulfonate, and benzoic acid. The choice of sodium xylenesulfonate was based on the fact that it was

listed in the literature as being very effective as well as economical. The ortho isomer was arbitrarily chosen. Benzoic acid was selected as the non-electrolyte because it is easily analysed for in the presence of neutral salts by titration with standard sodium hydroxide solution. Solubility data at 40°C. was also determined for systems in which sodium o-xylenesulfonate was replaced by sodium benzenesulfonate, sodium m-benzenedisulfonate, sodium p-toluenesulfonate, sodium m-xylenesulfonate, sodium p-cymenesulfonate, sodium p-bromobenzenesulfonate, and sodium cinnamate.

Experimental results are shown both in tabular form and graphically. After analysing the data, it was concluded that the solubility of benzoic acid in these solvents is due to a "salt effect" rather than to a solubilizing effect due to similarity in structure.

I INTRODUCTION

Hydrotropic solutions are aqueous salt solutions capable of dissolving substances normally either insoluble or slightly soluble in water at the same temperature. The hydrotropic substance, as well as the substance dissolved, may be either an organic or an inorganic compound. Further, an organic salt may act hydrotropically toward an inorganic compound - e.g., calcium sulfate scale dissolves in sodium benzoate solution - and an inorganic salt may act hydrotropically toward an organic compound - e.g., aniline is soluble in lithium chloride solution. In general, the organic compounds which act as hydrotropic substances are salts of the higher molecular weight organic acids, such as benzoic acid, aryl sulfonic acids, long chain fatty acids, etc. Neuberg (23) has presented extensive lists of both hydrotropic substances and substances which were dissolved. It is the usual case that a relatively concentrated salt solution is required to effect a marked change in solubility of the substance to be dissolved. Cresol is practically insoluble in water, but is completely miscible with a 40 percent aqueous sodium xylenesulfonate solution at 25°C (2). The dissolved substances are usually reprecipitated on dilution with water.

Theories of Hydrotropy

Hydrotropic solution is often described as a "salting-in" effect as opposed to the more commonly known "salting-out" effect, and several theories are based upon this line of reasoning. A study of these two effects together, called simply the "salt effect," has been reviewed by Gross (6). He points out that the individual ionic effects are additive. To explain this a theory of the antagonistic action of the cation and anion is proposed, and reasons are advanced that make it seem probable that the cation is responsible for the salting out portion and the anion for the salting in portion of the effect. According as one or the other predominates, in the case of a given electrolyte, a net observed salting out or salting in of a given non-electrolyte will result.

The salting out effect of cations decreases with increased size in the case of alkaline earth metal cations. The order of salting in of anions increases with size in the case of halides; conversely the salting out effect decreases. Linderstrom-Lang (12) found that sodium and lithium chlorides salted out boric acid, while potassium, rubidium and cesium chlorides salted it in.

Gross also states that substances which are most polar are least salted out from an electrolyte solution of fixed ion population and kind.

Debye (3) also treats salting-in and salting-out as opposing effects. The field around the ions of the hydrotropic salt may cause the aggregation of either water molecules or molecules of the non-electrolytes depending upon which has the greater polarity. The criterion of polarity is the dielectric constant of saturated aqueous solution of the non-electrolyte relative to water at the same temperature. If the saturated solution has a dielectric constant less than water, water molecules aggregate around the ions. This results in a reduction in solubility of the non-electrolyte (salting out) due to an increase in non-electrolyte-water ratio in regions of solution. If the dielectric constant of the saturated solution is greater than that of water, molecules of non-electrolyte aggregate around the ions. This reduces the non-electrolyte-water ratio in the regions of solution, thus increasing the solubility of the non-electrolyte (salting in). This theory seems to make hydrotropic solution dependent only upon the nature of the non-electrolyte and independent of the "hydrotropic" salt.

Some authors attribute hydrotropic solution to the formation of a compound soluble in water between the hydrotropic salt and the substance to be dissolved. An example of this is the increased solubility of iodine in a potassium iodide solution due to the formation of the compound, KI_3. Other authors rule out compound formation as a case of hydrotropic solution. This seems to be quite logical, since benzoic acid and many other insoluble acids are readily "dissolved" in sodium hydroxide solution due to the formation of their soluble sodium salts. These neutralization reactions are not considered to be cases of hydrotropic solution. Hence, compound formation may be ruled out as an explanation of hydrotropy by definition.

Bancroft (1) presents as an explanation of hydrotropy that the solution of hydrotropic salt in water acts as a mixed liquid solvent, the dissolved hydrotropic substance, whether it be solid, liquid, or gas, acting as a second liquid. This type of mixed solvent would be comparable to alcohol-water mixtures which are also used as solvents, in which solubility is due to the similarity in structure or polarity of alcohol and the third component.

Kuthy (9) suggests that the action of hydrotropic substances resembles that of emulsifying agents in that the hydrotropic substances act by presenting new physical conditions rather than new chemical complexes. The difference in behavior of hydrotropic substances toward different chemical substances, varying from solution and emulsification to salting out, are ascribed to differences in surface activity of the hydrotropic substances. The value of surface activity is a function of the polarity difference between the two phases and, hence, ultimately of the chemical structure.

Kruyt and Robinson (8) explained the increased solubility as due to the polar properties of the hydrotropic solution. Lindau (11) explained hydrotropic solution on a phase rule basis by considering the salt equivalent to a third miscible liquid.

There are many other explanations of hydrotropy, but at present there is no one generally accepted theory.

There is the possibility that all cases of abnormal solubility cannot be explained by one theory. That is to say, there may be different types of hydrotropic solution depending upon the nature of the non-electrolyte dissolved.

Correlation of Hydrotropic Data

Freundlich and Slottman (5) studied the solubility increase of benzoic acid and phthalic acid in the presence of sodium salts of benzene-, p-toluene-, and p-ethyl benzene sulfonic acids, in various concentrations. The dependence of the relative solubility increase, $\lambda = \frac{\Delta S}{S_o}$, upon the concentration of the hydrotropically active electrolyte, c, can be expressed through the formula $\lambda = \lambda_1 c^n$, where λ_1 and n are constants, the value of the latter ranging from 1.1 to 2.0. The concentrations of the different salts, equally effective in increasing the solubility bear a constant relation to each other.

Durand (4) has set up a similar equation expressing the relative increase in solubility to the normality of the hydrotropic solvent as follows:

$$\rho = AN^b, \text{ where}$$

N = normality of hydrotropic salt

A = index of hydrotropy

b = exponential coefficient of hydrotropy

$\rho = \frac{S-S_1}{S_o}$, where

S = solubility of solute in 1 liter of hydrotrope

S_1 = solubility of solute in 1 liter of aqueous NaCl solution of the same normality

S_o = solubility of the solute in 1 liter of water

A and b have different values for different hydrotropes and also for different solutes in the same hydrotrope.

An equation proposed by Setschenow (25) has been found to be applicable to the solubility of nitrobenzene and azobenzene in aqueous solutions of a mixture of sodium and potassium xylenesulfonates. The equation is as follows:

$$\log \frac{S_o}{S} = \log f_c = KC_s\text{, where}$$

S_o = solubility of non-electrolyte in weight units per volume of water.

S = solubility of non-electrolyte in weight units per volume of salt solution.

c_s = salt concentration in mols per liter.

K = salting out constant.

f_c = activity coefficient of the non-electrolyte in concentration units.

In the case of salting in K takes on a negative value - e.g. above K for nitrobenzene is -0.59 and K for azobenzene is -0.68.

Uses of Hydrotropic Solutions

The industrial applicability of hydrotropic solutions results from the fact that they increase the solubility of a large number of substances, which are normally either insoluble or slightly soluble in water. In almost all cases the use of hydrotropic solutions shows decided advantages over the use of other solvents.

The general type processes to which hydrotropic solutions are applicable are:

1. selective solvents in extraction processes,
2. reaction media for organic reactions,
3. crystallization media,
4. solvents in electrochemical reactions.

There are many examples of each of the above processes. In liquification of gases, the gas is dissolved in hydrotropic solution and driven off by heating prior to liquification. (14)

Both United States and Canadian patents have been obtained by R. H. McKee (15, 17, 18) for a process for the extraction of lignin from wood by means of hydrotropic solution to yield a high grade pulp. Sodium xylenesulfonate was found to be the most efficient as well as the most economical hydrotropic to use. A 30-40% salt solution is used in a digestor until it becomes saturated with lignin. The cellulose material containing lignin is cooked with the hydrotropic liquor at 150-160°C. for about twelve hours. The cellulose is filtered and washed with the hydrotropic solution. The cooking liquor is used six or seven times, and then the lignin is recovered by diluting with three volumes of water. The hydrotropic solution, after being reconcentrated, by evaporation, is used for successive cooks with no loss of effectiveness.

Lau (10) studied the extraction of lignin from bamboo pulp by a similar method and listed the following advantages: higher yield than by other processes, repeated use of the solution with simple and complete recovery, no evil smelling gas evolved and no difficulty in disposing of waste liquor, and no chemicals other than the hydrotropic solution are needed.

Aniline and dimethyl aniline which have similar boiling points and which are therefore very difficult to separate by distillation, may be separated by extracting the aniline with an aqueous calcium cymenesulfonate solution. As in the pulp process above, the solute may be recovered by dilution with water and the hydrotropic solution made ready for re-use by concentrating. (7, 18)

A sodium cymenesulfonate solution may be used to extract phenols and other "tar acids" from "tar oils." This eliminates the use of caustic soda and its neutralization. (13, 18)

A sodium bicarbonate solution may be used to extract beryllium hydroxide from a reaction mixture of beryl ore and caustic soda. This eliminates the use of troublesome concentrated acids. (16)

The following are examples of organic reactions in which hydrotropic solvents are used. Amines may be prepared from corresponding halides of hydrocarbons and substituted hydrocarbons by reacting these halides with ammonia in a hydrotropic solution. This involves the preparation of a hydrotropic solution containing ammonia to which an organic halide is added. The solution is subjected to heat and pressure to cause reaction and yields an amine hydrochloride. Excess ammonia and halide are removed by distillation and the remaining mixture is caustisized and the amines recovered by suitable means (distillation, filtration, etc.). (23)

If in the Cannizaro Reaction - conversion of benzaldehyde to benzoic acid and benzyl alcohol - a saturated sodium cymenesulfonate solution is used rather than a strong caustic soda solution, the yield of benzoic acid is 72.5% of theoretical in the former case as compared to 4.9% in the latter case. (18)

Good yields of dyes prepared by coupling reactions are obtained by using hydrotropic solutions instead of concentrated sulfuric acid to dissolve soluble reactants, such as diphenyl amine. (18)

The solubility and hydrolysis of mustard gas both were found to be increased by the use of hydrotropic solutions. (26)

Aqueous calcium cymenesulfonate solutions are used as crystallization media for the purification of sulfanilic, salicylic, and benzoic acids. In a similar manner slightly soluble amines can be recrystallized and the size of the crystals simultaneously controlled. (18)

There are numerous advantages of hydrotropic solvents over organic solvents in electrochemical reactions. These are as follows: (20, 22)

1. They are non-volatile, thus not subject to losses by evaporation. Evaporation of water would increase solvent action.
2. They are non-flammable.
3. They are good conductors themselves, thus require low cell voltage and low power consumption.
4. Owing to low voltages there is little heating of the solution by the electrolysis itself, so temperature control is easy.
5. They offer increased yields and current efficiency due to their general stability and property of dissolving the depolarizer.
6. No stirring is required.
7. They can be reused and operated in a continouous process. Separation of products, depending upon their nature, could be accomplished by distillation, extraction, dilution with water, or a combination of these, with reconcentration of the solvent by evaporation.
8. The solutions can be operated at any pH for either oxidation or reduction without the formation of tars.
9. A broad choice of cathodes and anodes is possible.

A common reduction reaction which may be carried out in this manner is the conversion of aromatic nitro compounds to the corresponding amines, amino phenols, or hydrazo compounds. The nature of the final reduction products depends primarily on the pH of the catholyte. In strongly acid solutions amino phenols are formed, in moderately acid solutions the reduction products are amines, and in alkaline solutions hydrazo compounds are obtained. On increasing the cathodic current density the yield of hydrazo compounds tends to decrease with formation of large proportions of amines, but this effect is counteracted by increasing the free alkali content in the catholyte. (21)

The electrolytic oxidation of benzaldehyde to benzoic acid in sulfonate solvents is carried out in the presence of a copper oxide catalyst at a nickel anode with high anode gas absorption efficiency and without tar formation under alkaline conditions. (22)

Statement of the Problem

There have been many hydrotropic salts, and non-electrolytes dissolved by aqueous solutions of these salts, reported in the literature. One of the earliest investigators in this field was Neuberg (23) who in 1916 published extensive lists of these compounds. Since that time, there have been many more articles published on various phases of hydrotropy including numerous examples of salts and non-electrolytes, theories, uses, physiological significance solubility data, etc. However, no complete phase equilibrium data of any three component system, water, hydrotropic salt, and non-electrolyte has ever been published. By complete phase equilibrium data is meant solubility data at various temperatures of the salt, the non-electrolyte, any compounds or double salts formed between them, and/or any hydrates in equilibrium with the aqueous solution of these compounds.

A complete phase diagram shows the composition of all saturated solutions and the solids in equilibrium with saturated solution, as well as showing equilibrium between solids. Once the diagram has been determined at various temperatures, it can be utilized in showing the effect of varying composition or temperature on the number of phases present. Thus, it is possible to determine if a third component would be reprecipitated from hydrotropic solution on dilution with water. The amount precipitated could also be predicted.

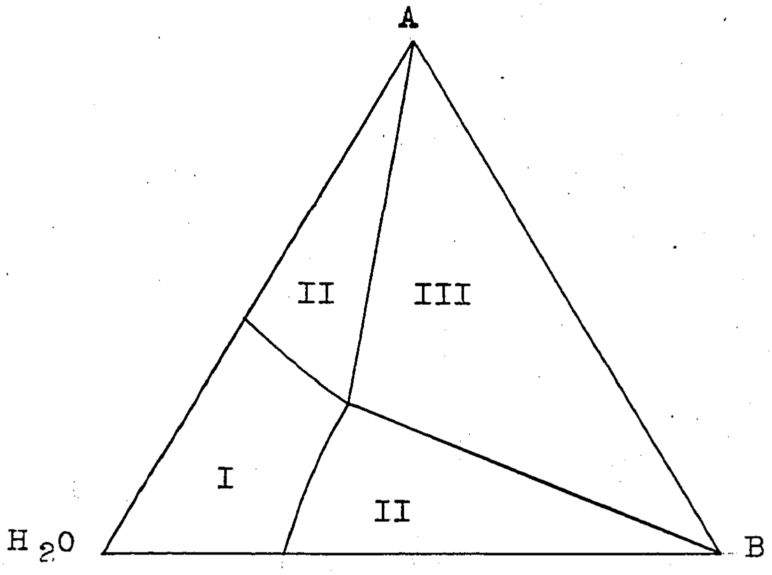
It was the object of this research, first, to investigate the phase equilibria data for the system, water, sodium o-xylenesulfonate and benzoic acid, at several temperatures. Sodium xylenesulfonate was chosen as the hydrotropic salt because it is frequently encountered in the literature as an example of a very effective as well as relatively inexpensive hydrotrope. The 4-isomer of o-xylene was arbitrarily selected. Benzoic acid was chosen as the non-electrolyte because it offers an easy means of analysis in that it may be titrated with sodium hydroxide solution using phenolphthalein as indicator. Sodium xylenesulfonate, a salt of a strong acid and strong base, is essentially neutral and should offer no interference. This was found to be true. Benzoic acid is only slightly soluble in water, but, as reported in the literature, its solubility is increased appreciably in sodium xylenesulfonate solutions.

As an additional part of the research the solubilizing effect of several other similar salts on benzoic acid was investigated with the idea of looking into the possibility of correlating increased or decreased hydrotropic effect depending upon the structure and molecular weight of the salt.

Before attacking the problem experimentally, it is well to look into the possible phase diagrams that might arise. The data is represented on triangular coordinates and consists of weight percentages of the three components in solutions of various concentrations in equilibrium with excess solids at a given temperature. In this method of representing percentages, an equilateral triangleis used, each vertex of which represents a pure component. The side opposite a vertex represents zero percent of that component, ar all mixtures of the other two components alone. Equally spaced lines parallel to the side represent linear increases in percentage of that component. Any mixture of the three components may be represented by a single point within the triangle.

The following figures represent the cases which are commonly encountered. The Roman numerals inside the diagram denote the number of phases present in that particular region. The boundaries of the one phase regions are determined by analyzing various concentrations of solutions in equilibrium with excess solids. The tie lines may be determined by the "wet-residue" method. This consists in analyzing the moist solids in equilibrium with the solution at two different concentrations. The two lines joining the points representing the corresponding concentrations of the solution and of the moist solids, and extended past the latter points, intersect at a point representing the solids in equilibrium with solution.

Case I - No compound, double salt, or hydrate formation. The solutions are in equilibrium with the anhydrous solids only.

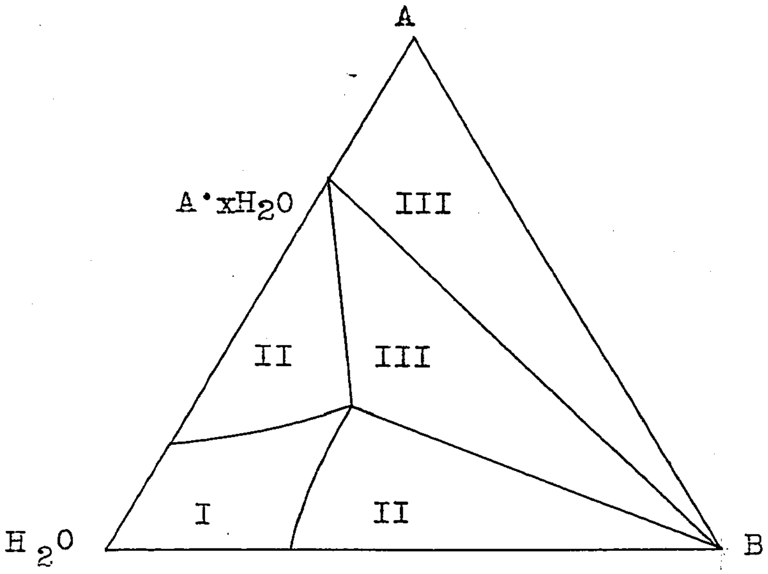


I - Unsaturated solutions of A and B in H_2O.

II - Saturated solutions in equilibrium with solid A or B.

III - Solution saturated with respect to A and B, in equilibrium with solid A and B.

Case II - Hydrate formation in one solid phase.

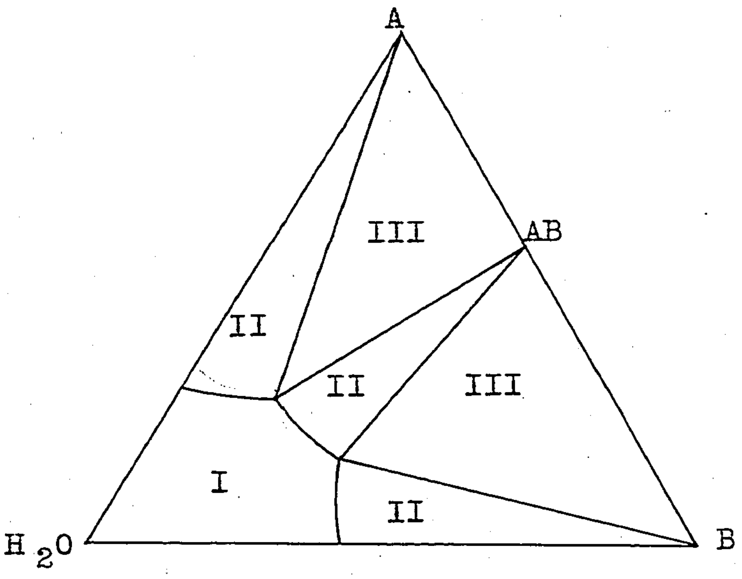


I - Unsaturated solutions of A and B in water.

II - Saturated solutions in equilibrium with solid B or a hydrate of solid A.

III - Solid B and a hydrate of solid A in equilibrium with solid A or saturated solution with respect to A and B.

<u>Case III</u> - Compound or Double Salt Formation.

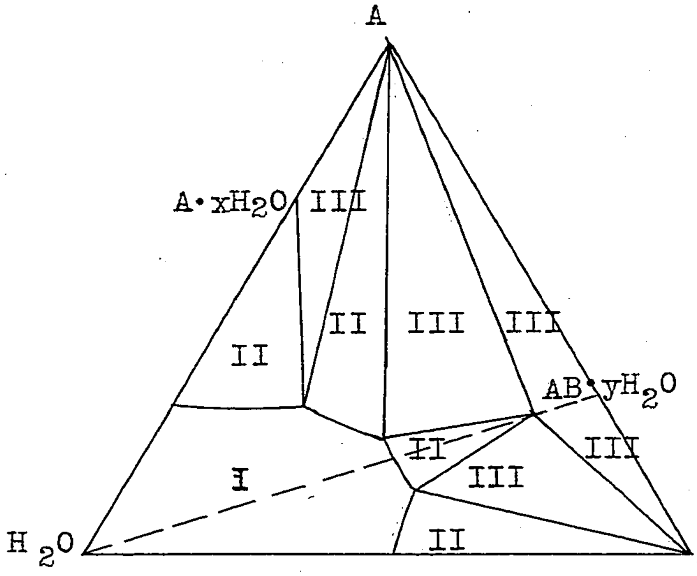


I - Unsaturated solutions of A and B in water.

II - Saturated solutions in equilibrium with solid A, solid B, or double salt AB.

III - Saturated solution and double salt AB in equilibrium with solid A or solid B.

<u>Case IV</u> - Combinations of the above cases. (Example: System containing a hydrate of A, a double salt AB, and a hydrate of the double salt.)



I - Unsaturated solutions of A and B in water.

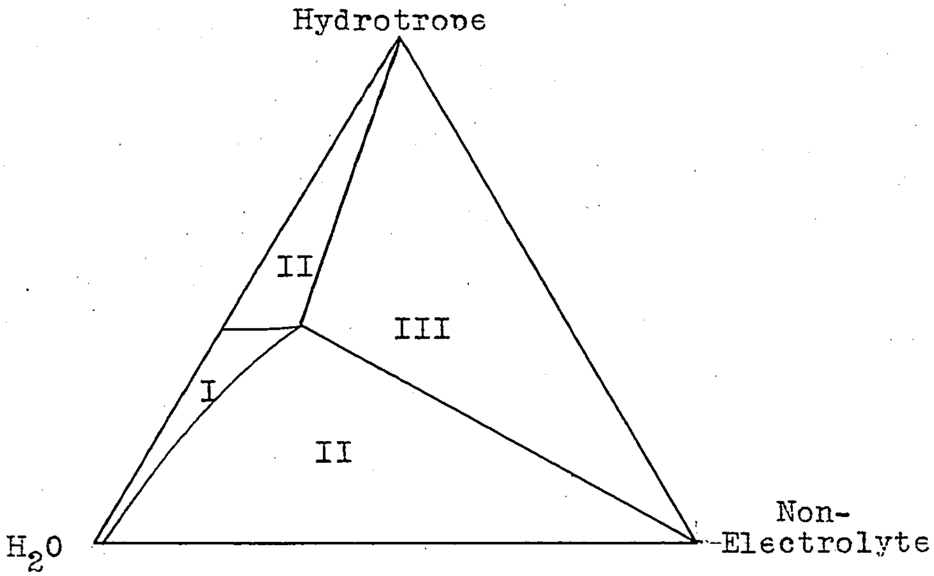
II - Saturated solutions in equilibrium with a hydrate of solid A, solid A, a hydrate of double salt AB, or solid B.

III - (a) Saturated solution and solid A in equilibrium with a hydrate of solid A or a hydrate of double salt AB.

(b) Double salt AB, a hydrate of double salt AB in equilibrium with solid A or solid B.

(c) Equilibrium between solid B, a hydrate of double salt AB, and saturated solution.

The preceding diagrams represent the general cases where the solubility of both solids in water is average. In the case of hydrotropic solution the following type of diagram might be expected, the pure non-electrolyte being almost insoluble in water with its solubility increasing with added hydrotropic substance. This diagram shows the case in which no hydrates or compounds are in equilibrium with the saturated solution. This was arbitrary and should not infer that these other conditions cannot exist.



After determining the phase equilibria for a given system, several preliminary interpretations may be made depending upon the number of portions of the curve bounding the one phase region. Two portions occur when there exists two anhydrous substances, an anhydrous substance and a hydrate, or two hydrates along with water. Three portions indicate the possibility of double salt or compound formation in addition to the pure substances or their hydrates.

II EXPERIMENTAL

Phase equilibrium data was obtained for the system, water, benzoic acid, and sodium o-xyelensulfonate at 30°C, 40°C, and 60°C. This consisted in determining the solubility of benzoic acid in aqueous solutions of various concentrations of sodium o-xylenesulfonate, as well as the solubility of sodium o-xylenesulfonate in aqueous solutions of various concentrations of benzoic acid, and the composition of the solid phase in equilibrium with these solutions.

Additional data was obtained at 40°C for the solubility of benzoic acid in aqueous solutions of various concentrations of the following salts: sodium benzenesulfonate, sodium p-toluenesulfonate, sodium m-xylenesulfonate, sodium p-cymenesulfonate, sodium p-bromobenzenesulfonate, sodium p-phenolsulfonate, sodium m-benzenedisulfonate, and sodium cinnamate. C. P. benzoic acid was used and the hydrotropic salts were the best grades obtainable from Eastman Kodak Co. and Wyandotte Chemicals Corp.

The determinations for the system involving sodium o-xylenesulfonate were made in the following manner.

<u>Procedure for making up solutions</u>. Saturated solutions of benzoic acid in aqueous sodium o-xylenesulfonate solutions, and of sodium o-xylenesulfonate in aqueous benzoic acid solutions were made up by having benzoic acid and sodium o-xylenesul-

fonate in excess, respectively.

The ingredients, roughly weighed out and enough to make up about 100 grams of solution, were placed in a stoppered 125 ml. erlenmeyer flask. This mixture was heated to a temperature above that of the determination, but not to boiling, in order to dissolve all or nearly all of the solid material. The solution was then cooled and placed in a constant temperature bath and allowed to come to equilibrium.

The solution was stirred from time to time, and 24 - 48 hours were allowed to insure equilibrium. If excess solid material did not separate out on cooling, additional material was added and the above procedure repeated.

The bath consisted of a five gallon battery jar filled with distilled water. The temperature was controlled to ± 0.2°C with an American Instrument Co. bimetallic thermostatic control device, and was measured by means of a mercury thermometer graduated to 0.2°C. At first, some trouble was encountered in controlling the temperature within the desired range because of a decrease in water level due to evaporation. This problem was almost completely eliminated by the use of a layer of mineral oil on top of the water.

After equilibrium was considered to have been reached, five portions of supernatant saturated solution of 3 - 5 ml. each were drawn off by means of a pipette, the flask remaining in the constant temperature bath. After removal of these samples, an additional amount of sodium o-xylenesulfonate (or benzoic acid) was added to the remaining mixture to produce the desired incremental increase in concentration, and the above procedures repeated. In the determination of the solubility of benzoic acid in aqueous sodium o-xylenesulfonate solutions the initial concentration of the salt used was 10 - 15% and its concentration was increased in increments of 5 - 10% until the solution became saturated with both substances. In the determination of the solubility of sodium o-xylenesulfonate in benzoic acid solutions the initial concentration of benzoic acid was 5% or less and the increments of increase were smaller than above. Thesolubility of pure sodium o-xylenesulfonate in water was determined at 30°, 40°, and 60°C, and the solubility of benzoic acid in water was determined at 60°. The solubility of benzoic acid in water at 30° and 40° was obtained from the literature(26).

<u>Procedure for analyzing solutions</u> - The portions of saturated solution were transferred to ground glass covered tared weighing bottles. The evaporation of water was considered to be negligible during transfer and the weight of saturated solution was obtained by difference.

Benzoic acid was determined by titration with standard sodium hydroxide solution. Values of normality of the different sodium hydroxide solutions used ranged between .0498 and .1331. These solutions were standardized against weighed samples of pure dry potassium biphthalate with a precision of 2 parts per thousand. Two liters of solution were made up at a time, and since this was not consumed for several weeks, the normality was checked from time to time. Three portions were titrated directly in the weighing bottles, using phenolphthalein as indicator. This is the standard method for the determination of the neutralization equivalent of weak acids such as benzoic acid. A blank determination was performed on an aqueous sodium o-xylenesulfonate solution. One drop of base was sufficient to produce a pink color with phenolphthalein.

A fifty milliliter buret graduated in tenths of a milliliter and read to hundreths of a milliliter was used in the titrations. The calculated values of percent benzoic acid were considered to be in good agreement if they differed by no more than .02 - .03 percent. For a sample containing approximately five percent benzoic acid, this difference would mean a precision of 4 - 6 parts per thousand. A five gram sample containing five percent benzoic acid requires 20 ml. of 0.1N base to neutralize the acid. Therefore, the above precision is obtained by reading the buret with an accuracy of ±.05 ml., or a range of a tenth of a milliliter.

Most samples titrated weighed between three and six grams. The higher the benzoic acid content, the smaller the sample used in order to keep the titrations less than 40 ml. Since the volume of base required increases directly with percent benzoic acid, the precision required in all titration would be expected to remain approximately the same as above - i.e. an accuracy of reading the buret to ±.05 ml. should give percentages of benzoic acid which check to .02 - .03 percent for all ranges of concentration of benzoic acid. Actually greater precision was obtained for the lower percentages of benzoic acid since larger samples were used.

The remaining two portions of saturated solution were placed in a drying oven at a temperature of 110 - 120°C. At this temperature the water was driven off by evaporation and benzoic acid was removed by sublimation. The samples were left in the oven until a constant weight was obtained on two successive weighings. The weighings were made at about 48 hour intervals. The samples reached constant weight within 4 - 6 days as a rule.

Since pure chemicals were used, the dried residue was assumed to be only sodium o-sylenesulfonate, the amount of water was obtained by difference. The results are expressed as weight percent of each component.

Sample Data Sheet

Weighing bottle	1	2	3
Wt. empty	31.5583	33.9368	30.5336
Wt. plus sample	36.6523	37.8723	35.7392
Wt. of sample	5.0940	3.9355	5.2056
Ml. of NaOH	25.80	19.96	26.43
% Benzoic Acid (BzOH)	5.60	5.60	5.61

Ave. % BzOH = 5.60

$$\% \text{ BzOH} = \frac{\text{ml. NaOH} \times \text{N}\cdot\text{NaOH} \times \frac{\text{Mol.wt. BzOH}}{1000}}{\text{weight of sample}} \times 100$$

Weighing bottle	4	5
Wt. empty	31.8513	31.6632
Wt. plus sample	37.5178	38.4464
Wt. of sample	5.6665	6.7832
Wt. plus dried sample	34.2838	34.5773
	34.2819	34.5741
to constant wt.	34.2819	34.5738
Wt. of dried sample	2.4306	2.9106
% sodium o-xylenesulfonate	42.89	42.91

Ave. % sodium o-xylenesulfonate = 42.90

$$\% \text{ sodium o-xylenesulfonate} = \frac{\text{wt. of dried sample}}{\text{wt. of sample}} \times 100$$

% water = 100 - (%benzoic acid +%sodium o-xylenesulfonate)

Procedure for Analyzing Wet Residues: The composition of solid sodium o-xylenesulfonate in equilibrium with saturated solution was determined by the wet residue method. (see page 14). The moist solids were recovered and sampled as follows: as much supernatant saturated solution was removed as possible by means of a pipette, the flask remaining in the constant temperature bath. In order to obtain uniform samples, the stoppered flask containing the moist solids was heated over a bunsen flame until all went into solution. Samples were then poured off into weighing bottles and analyzed as above.

There is no known hydrate of benzoic acid, hence it was not necessay to determine the composition of solid benzoic acid in equilibrium with saturated solution.

<u>Analysis of other systems</u>: The same type of analysis was applicable in the case of all other hydrotropic salts used. Only solutions saturated with respect to benzoic acid were analyzed. Hence, it was not necessary to analyze any solid residues.

The following salts were used in these determinations: sodium benzenesulfonate, sodium p-toluenesulfonate, sodium m-xylenesulfonate, sodium p-cymenesulfonate, sodium p-bromobenzenesulfonate, sodium m-benzenedisulfonate and sodium cinnamate.

Solubility data for the system benzoic acid, sodium p-bromobenzenesulfonate, water was determined in the above manner. However, after completion of this work, it was found that the original sodium, p-bromobenzenesulfonate was not pure. It contained an acid impurity as indicated by the fact that it was necessary to add a considerable volume of approximately 0.1N sodium hydroxide solution to an aqueous solution of the salt to produce a pink color with phenolphthalein. Rather than discard the above data, it was decided to determine if the acidity of the impure salt was constant throughout the lot of it. This acidity affected the benzoic acid determination, since the total acidity was assumed to be benzoic acid.

The volume of standard sodium hydroxide solution required to neutralize a gram of several samples of the salt was found to be constant (2.42 ml. of .1331 N base). The volume of sodium hydroxide was converted to milliequivalents of sodium hydroxide (or free acid) by multiplying by the normality of the sodium hydroxide solution used. The percentage of benzoic acid was corrected as follows:

$$\%\ \mathrm{BzOH} = \frac{\left\{\text{(vol. of NaOH to neutralize hydrotropic soln.)} \times (\mathrm{N \times NaOH}) - \text{wt. sample} \times \%\,\mathrm{NaBrBS} \times \frac{\text{meq. NaOH}}{\text{gm. NaBrBS}}\right\} \text{M.W. BzOH}}{\text{Weight sample}} \times 100$$

Thus, the hydrotropic effect was not determined for pure sodium p-brombenzenesulfonate, but for the salt with free acid present. Calculated as p-bromobenzenesulfonic acid, the salt contained 7.63 percent free acid by weight. This value would be lower if the acid present was of lower molecular weight.

In the determination of the solubility of benzoic acid in aqueous sodium p-cymenesulfonate solutions the analysis for the salt proved to be slightly uncertain. The time required for evaporating a sample to dryness and to constant weight was much longer than that for the other salts. As much as a month was required in the case of samples high in benzoic acid . This indicates that benzoic acid is more difficult to remove by sublimation from these solutions than from the others. There was also a gradual darkening of the salt during this time, an indication that decomposition was taking place. This was further indicated by the fact that after constant weight was reached, the residue was acid to phenophthalein. The original salt was neutral, as evidenced by the fact that only one drop of approximate 0.1 Normal base added to an aqueous solution of the salt was required to produce a pink color with phenolphthalein.

Although this data is not as precise as that obtained in most of the other determinations, it gives a good indication of the hydrotropic effect of sodium p-cymenesulfonate toward benzoic acid.

III RESULTS AND CONCLUSIONS

The phase equilibria data for the system benzoic acid, sodium o-xylenesulfonate, and water at 30°, 40° and 60°C as abtained from the analytical procedure is expressed as weight percent of each of the components. This data was also transformed by mathematical manipulation so as to express the solubilities in various ways. The experimental results are tabulated numerically in the appendix and are shown graphically in figures 1, 2, 3, and 4.

Figure 1 shows a plot of weight percent benzoic acid versus weight percent sodium o-xylenesulfonate on rectangular coordinates. Experimental points are shown on this plot, but have been omitted on all subsequent derived plots.

The same type of data is plotted on a triangular diagram in figure 2. In figure 3 complete phase equilibria at 60° C is shown with the various regions labeled. Experimentally determined tie lines in the sodium o-xylenesulfonate-water region are shown in figure 4.

Upon inspection of these plots, the following observations were made:

1. There is a pronounced increase in hydrotropic effect with increase in temperature. This seems to correspond with the relative increase in solubility of benzoic acid in water with temperature. A plot of the ratio of the solubility of benzoic acid in sodium o-xylenesulfonate solution

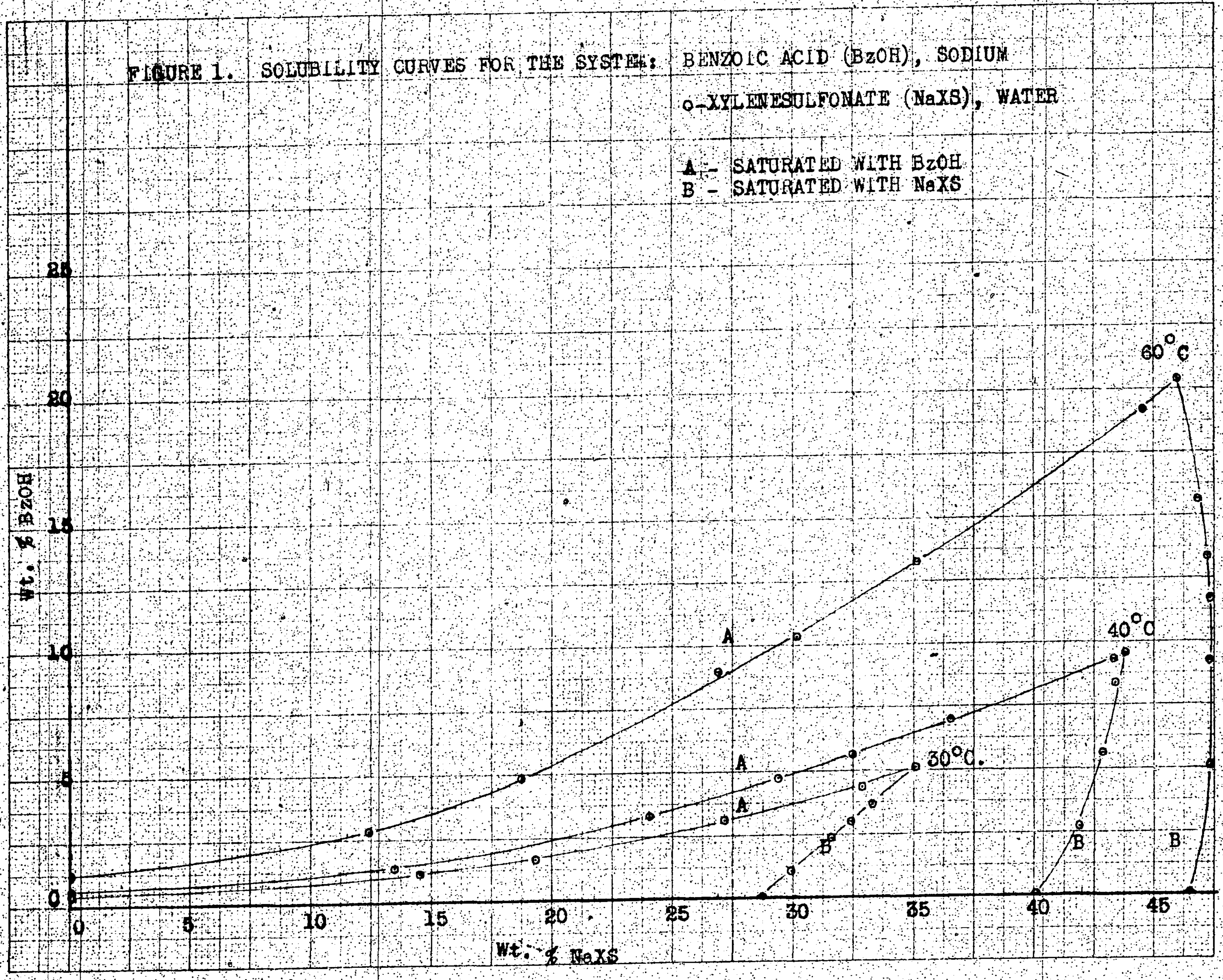


FIGURE 1. SOLUBILITY CURVES FOR THE SYSTEM: BENZOIC ACID (BzOH), SODIUM o-XYLENESULFONATE (NaXS), WATER

FIGURE 2: SOLUBILITY CURVES FOR THE SYSTEM
BENZOIC ACID (BzOH), SODIUM
o-XYLENESULFONATE (NaXS), WATER
(WEIGHT PERCENT OF EACH COMPONENT)

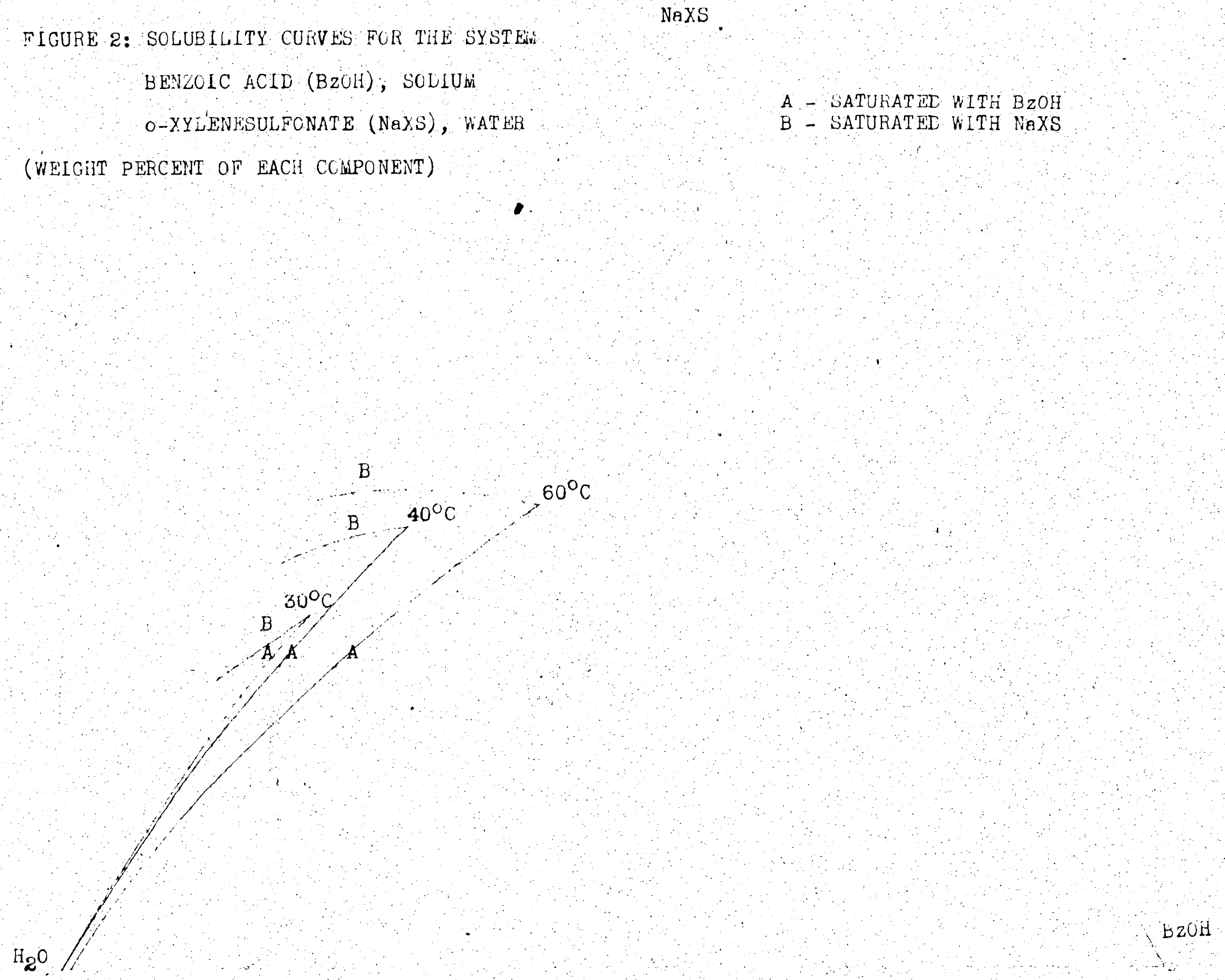
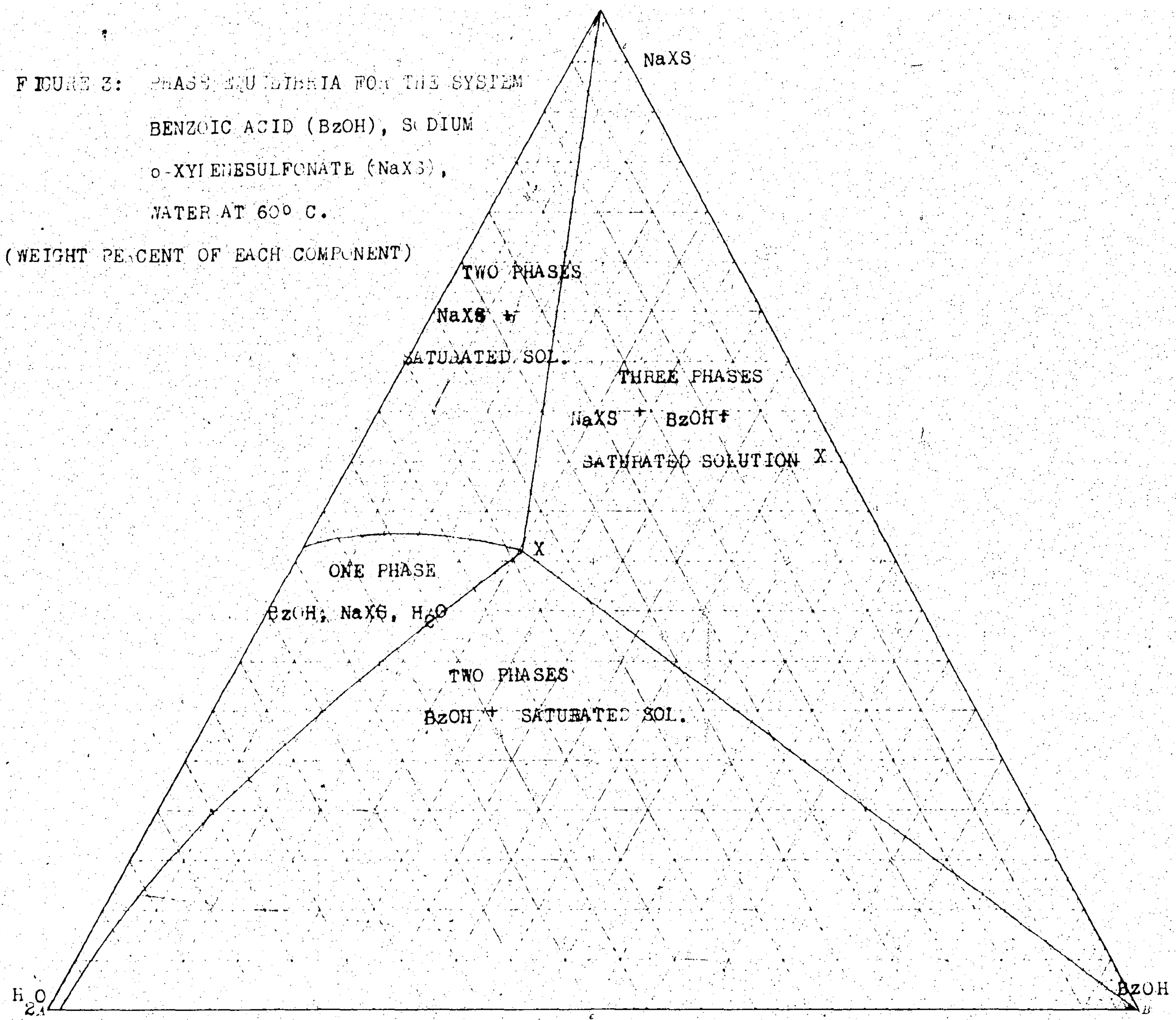


FIGURE 3: PHASE EQUILIBRIA FOR THE SYSTEM
BENZOIC ACID (BzOH), SODIUM
o-XYLENESULFONATE (NaXS),
WATER AT 60° C.
(WEIGHT PERCENT OF EACH COMPONENT)



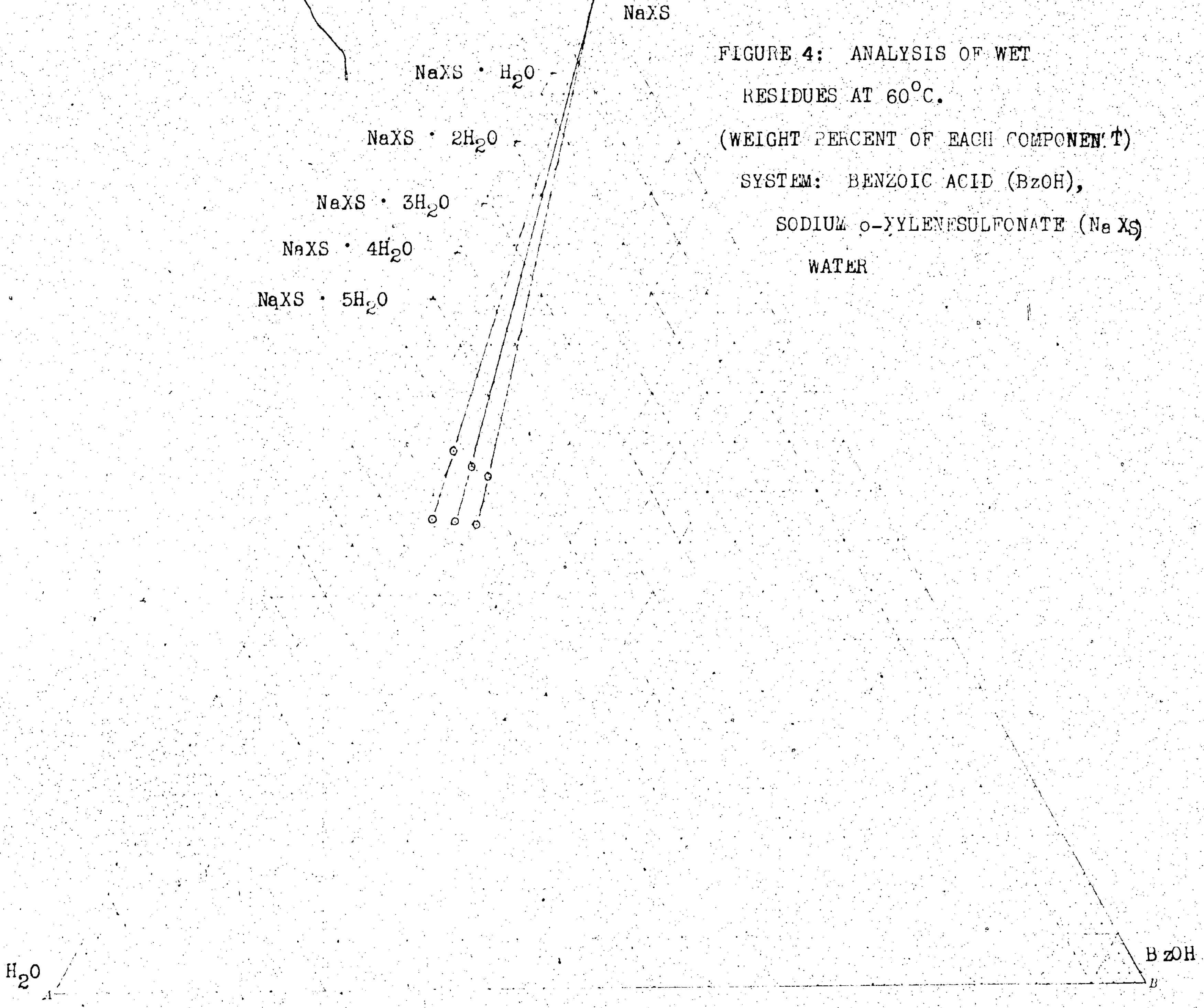


FIGURE 4: ANALYSIS OF WET
RESIDUES AT 60°C.
(WEIGHT PERCENT OF EACH COMPONENT)
SYSTEM: BENZOIC ACID (BzOH),
SODIUM o-XYLENESULFONATE (NaXS)
WATER

(weight percent benzoic acid in solution) to the solubility of benzoic acid in water (weight percent benzoic acid in solution) at the same temperature versus concentration of sodium o-xylenesulfonate (weight percent salt in solution) bears out the statement, in that the three curves practically coincide. (See figure 5).

2. The maximum concentration of benzoic acid in saturated solutions at 60° C is 20.39%. In this solution there is about 1 1/3 times as much sodium o-xylenesulfonate present as there is water.

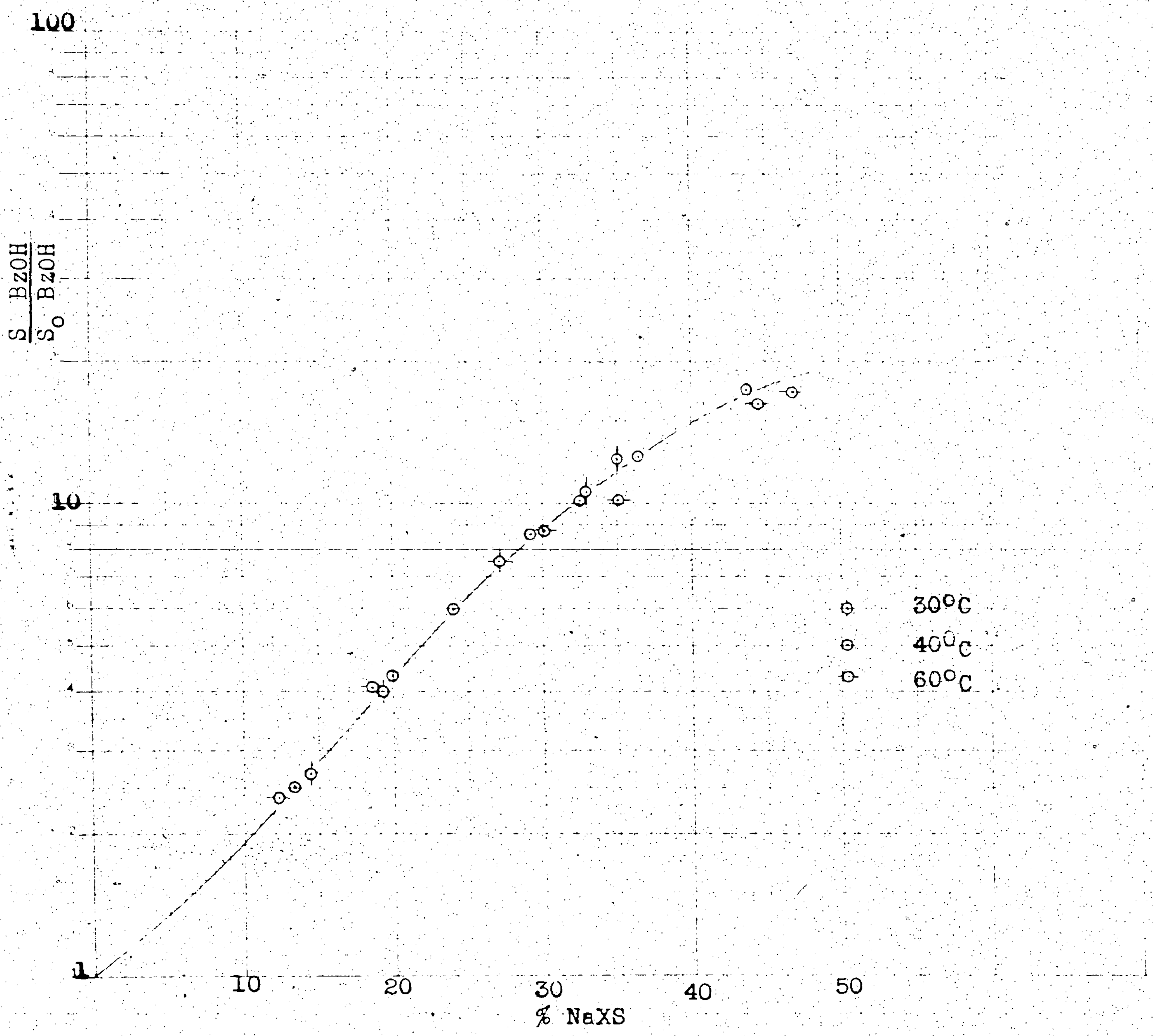
3. The maximum concentration of benzoic acid in saturated solutions at 40° C is 9.54%. In this solution there is almost as much sodium o-xylenesulfonate present as there is water.

4. At 30°C and 40°C the concentration of sodium o-xylenesulfonate in saturated solutions increases with increased benzoic acid concentration. However, the concavity ofthe curves representing these solutions is reversed at the two temperatures. At 60°C there is a maximum in the curve representing the concentration of sodium o-xylenesulfonate in saturated solutions. However, as shown in figure 7, by expressing the concentrations of sodium o-xylenesulfonate and benzoic acid in mols. per 1000 grams of water, the solubility of sodium o-xylenesulfonate increases with increasing concentration of benzoic acid.

FIGURE 5: RATIO OF SOLUBILITY OF BENZOIC ACID (BzOH) IN AQUEOUS SODIUM o-XYLENESULFONATE (NaXS) SOLUTIONS TO SOLUBILITY OF BENZOIC ACID IN WATER AT 30°, 40° AND 60°C.

- VERSUS -

% NaXS IN SOLUTION



5. The rate of increase of solubility of sodium o-xylenesulfonate in benzoic acid solutions with increasing temperature decreases with increasing temperature. This is also true for aqueous solutions.

6. The addition of water to an aqueous mixture is represented graphically on a triangular diagram by a line joining the points representing the composition of the solution and the water vertex. The more water added, the closer the point representing the resulting composition approaches the water vertex. Addition of water to the very concentrated solutions of benzoic acid in aqueous sodium o-xylenesulfonate solution produces composition in the two phase, benzoic acid-water, region. Thus, benzoic acid is precipitated out by dilution with water.

7. Since there are only two portions to the curve bounding the one phase region , there is no compound formation indicated between benzoic acid and sodium o-xylenesulfonate.

8. At 60° anhydrous sodium o-xylenesulfonate exists in equilibrium with saturated solutions. Referring to figure 4, it can be seen that in order for the lines drawn connecting the experimental points to intersect at any of the points representing hydrates of the salt, it would be necessary to rotate them through larger angles than are warranted by experimental accuracy. Thus, the possibility of the existence of a hydrate of the salt at 60° C. is eliminated.

At 30° and 40° a graphical analysis would be inaccurate, since lines joining points representing compositions of saturated solution and wet residues would necessarily approach the zero percent benzoic acid line at a very small angle. Thus, by shifting the line only a small amount, the anhydrous salt, or any of the lower hydrates might be indicated.

The derived plots are as follows:

1. Solubility of benzoic acid versus solubility of sodium o-xylenesulfonate, both expressed as mols per 1000 grams of solution. (figure 6).

2. Solubility of benzoic acid versus solubility of sodium o-xylenesulfonate, both expressed as mols per 1000 grams of water. (figure 7).

3. Solubility of benzoic acid in grams per 1000 grams of sodium o-xylenesulfonate solution versus concentration of sodium o-xylenesulfonate in mols per 1000 grams of sodium o-xylenesulfonate solution. (figure 11).

4. Solubility of benzoic acid in grams per 1000 grams of sodium o-xylenesulfonate solution versus weight percent sodium o-xylenesulfonate in sodium o-xylenesulfonate solution (figures 13 and 14).

5. Grams of benzoic acid per gram of sodium o-xylenesulfonate corrected for the amount of benzoic acid dissolved in the water present versus concentration of sodium o-xylenesulfonate in mols per 1000 grams of water. (fig.15).

FIGURE 6: SOLUBILITY CURVES FOR THE SYSTEM: BENZOIC ACID (BzOH), SODIUM o-XYLENESULFONATE (NaXS), WATER

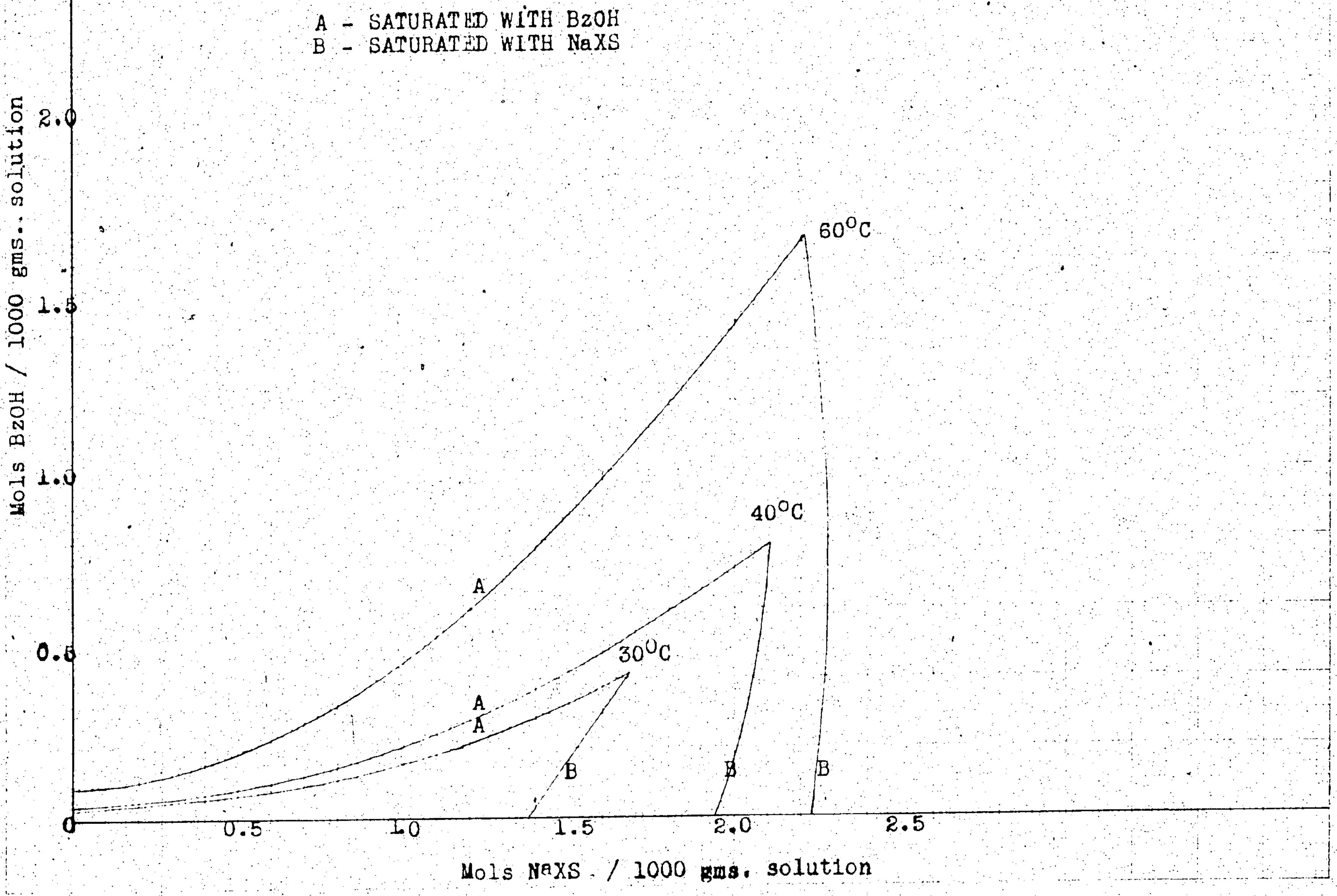
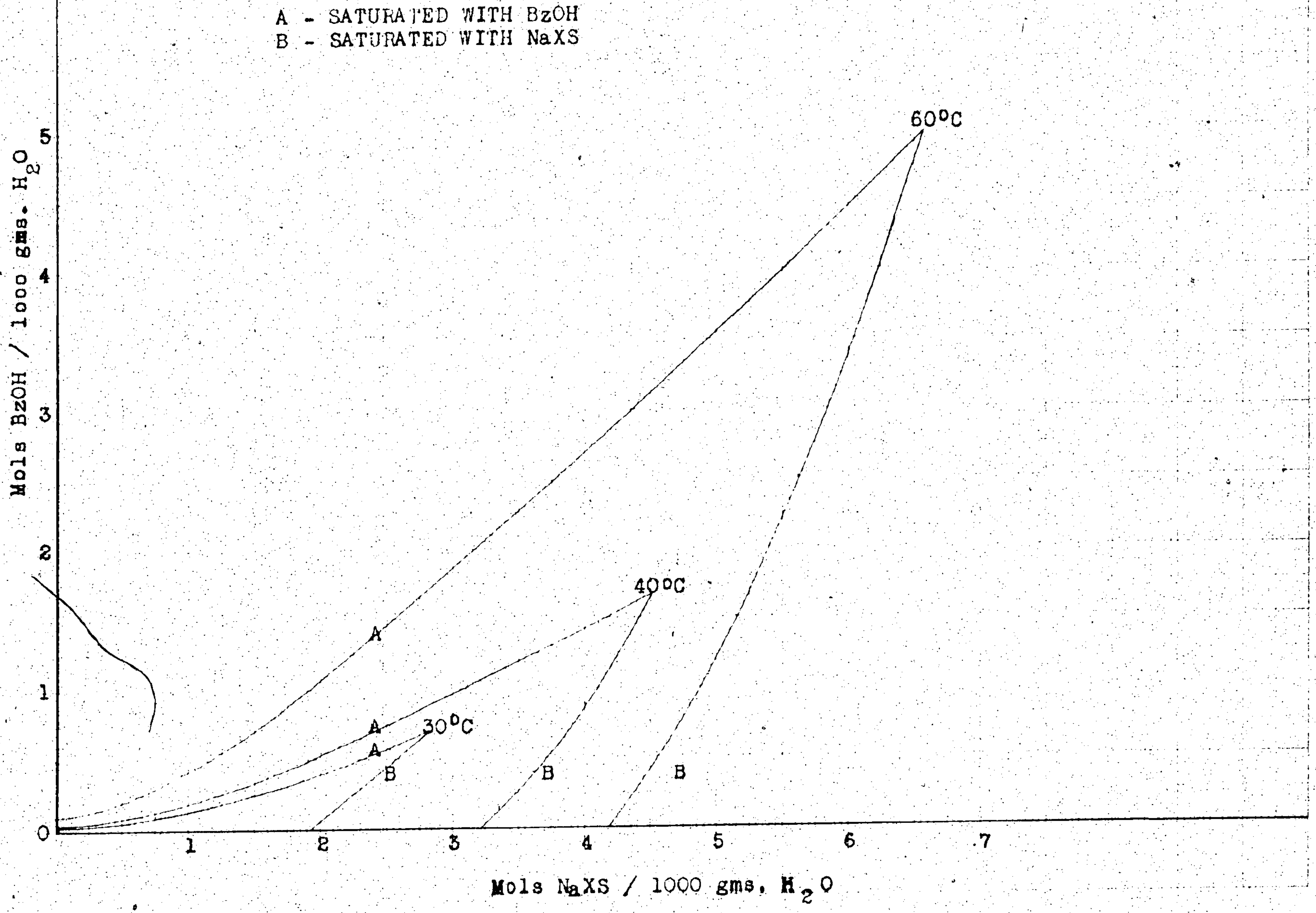


FIGURE 7: SOLUBILITY CURVES FOR THE SYSTEM: BENZOIC ACID (BzOH) SODIUM o-XYLENESULFONATE (NaXS), WATER



Results of the determinations of the solubility of benzoic acid in aqueous solutions of sodium benzenesulfonate, sodium p-toluenesulfonate, sodium m-xylenesulfonate, sodium p-bromobenzenesulfonate, sodium p-cymenesulfonate, sodium m-benzenesulfonate and sodium cinnamate at 40° are tabulated in the appendix. There was found to be a slight decrease in the solubility of benzoic acid in the sodium m-benzedisulfonate and sodium cinnamate solutions as compared to its solubility in water at 40°. Hence, extensive data was not obtained for these salts and these runs are not represented graphically.

The results of the determinations involving the other salts are shown graphically in comparison with the solubility of benzoic acid in aqueous sodium o-xylenesulfonate at 40° in figures 8 and 9. The results for the first three salts above were recalculated in terms of mols of benzoic acid per 1000 grams of water and mols of salt per 1000 grams of water and plotted as ordinate and abcissa, respectively. This plot also includes the corresponding curve for sodium o-xylenesulfonate and is shown in figure 10. Since there was a question as to the accuracy of the analysis for sodium p-bromobenzenesulfonate and sodium p-cymenesulfonate, similar recalculations were not carried out for these salts.

Of the six salts showing a hydrotropic effect toward benzoic acid, sodium p-cymenesulfonate was found to be

FIGURE 8: SOLUBILITY OF BENZOIC ACID (BzOH) IN HYDROTROPIC SALT SOLUTIONS AT 40° C.

(WEIGHT PERCENT OF EACH COMPONENT)

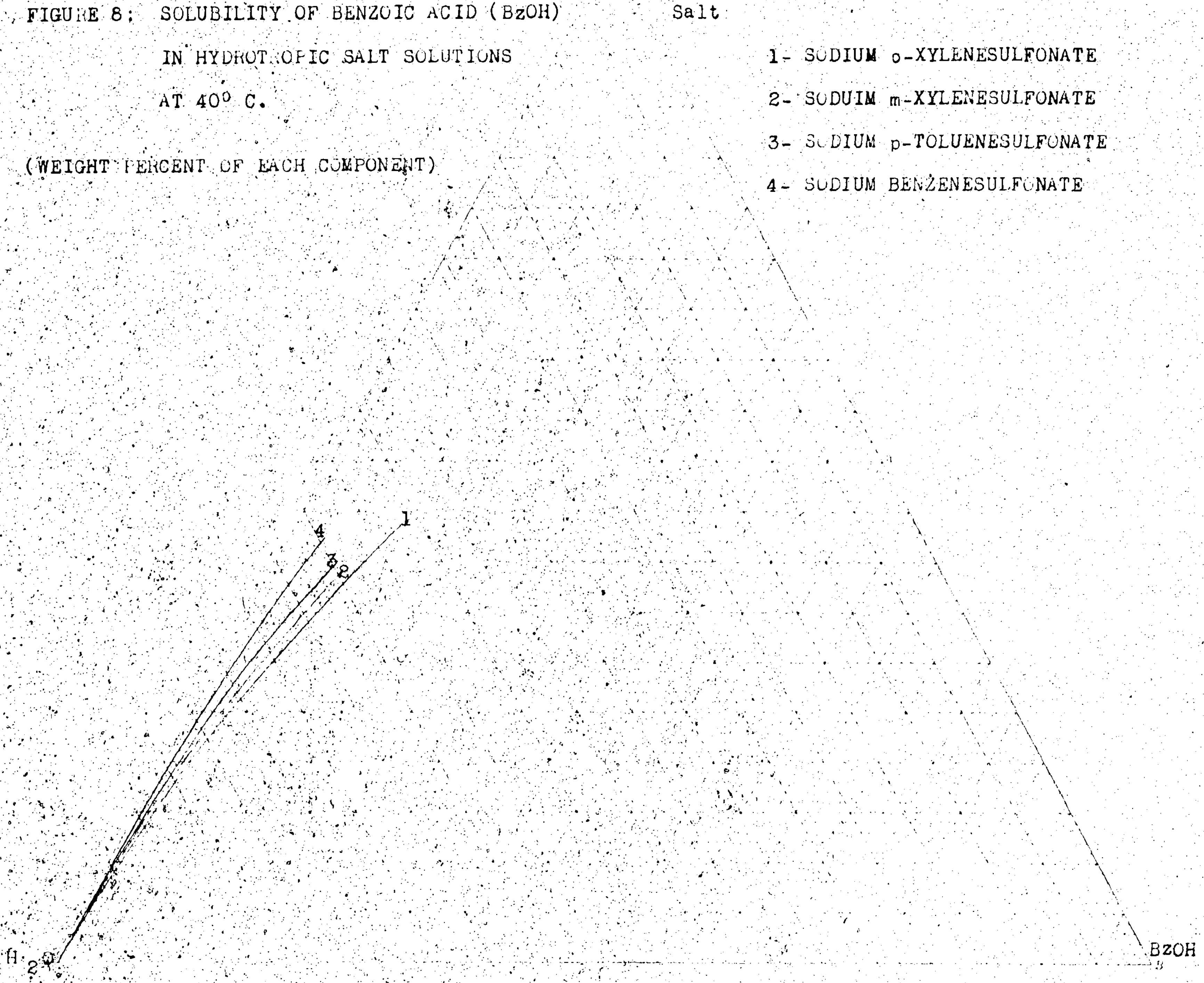


FIGURE 9: SOLUBILITY OF BENZOIC ACID(BzOH) IN HYDROTROPIC SALT SOLUTIONS AT 40°C.

(WEIGHT PERCENT OF EACH COMPONENT)

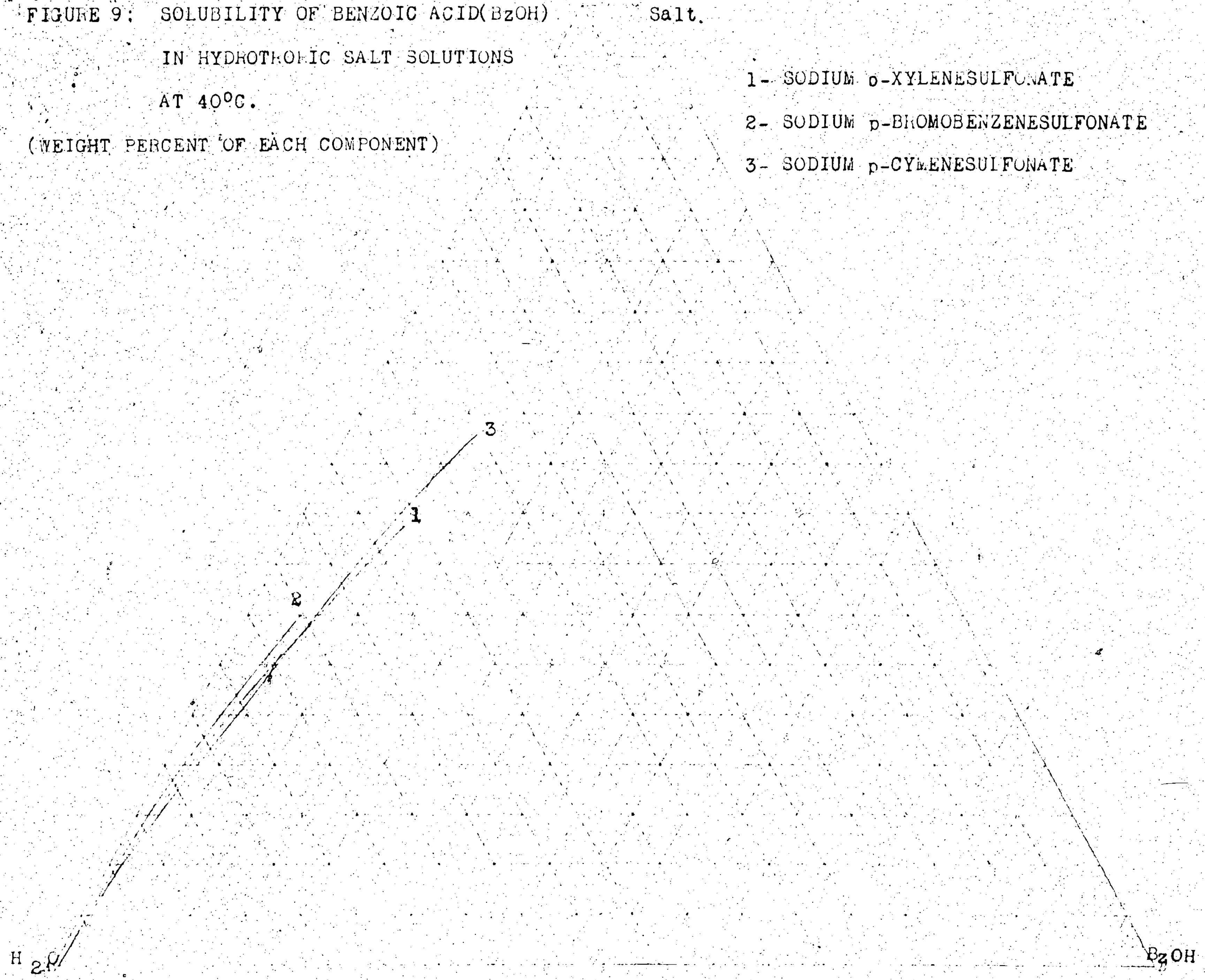
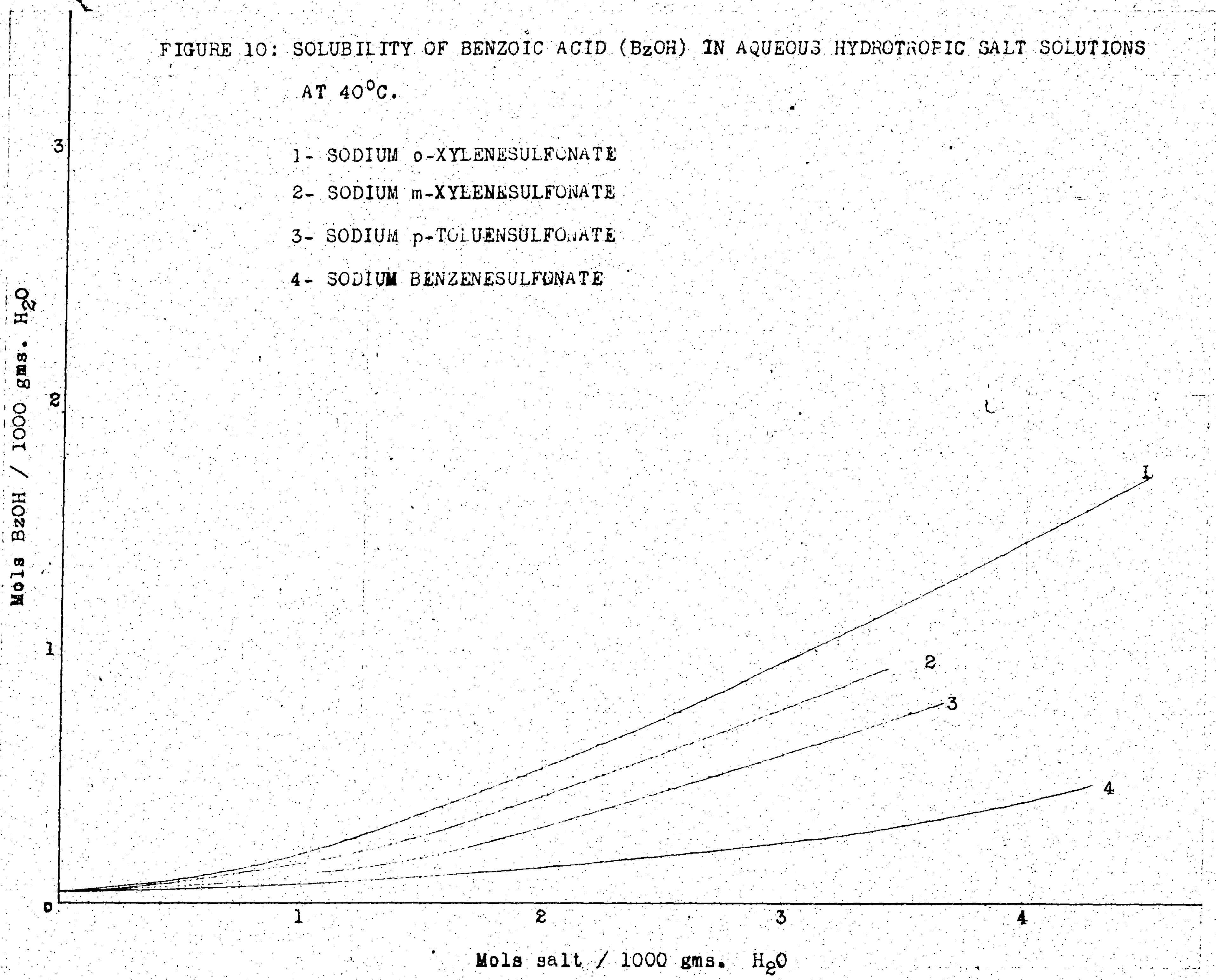


FIGURE 10: SOLUBILITY OF BENZOIC ACID (BzOH) IN AQUEOUS HYDROTROPIC SALT SOLUTIONS AT 40°C.



the most effective. A list of the others in order of decreasing effectiveness is as follows: sodium o-xylenesulfonate, sodium m-xylenesulfonate, sodium p-bromobenzenesulfonate, sodium p-toluenesulfonate, and sodium benzenesulfonate. In the absence of free acid it is entirely possible that sodium p-bromobenzenesulfonate would be more effective then sodium m-xylenesulfonate.

Thus, for the homologous series of derivatives of sodium benzenesulfonate, the hydrotropic effect toward benzoic acid increases with increased number and increased size of alkyl groups on the benzene ring. That is to say, the effect increases with increasing molecular weight and increaseing size of the molecule. The presence of a bromine atom on the ring yields a molecule of approximately the same size as if a methyl group was present. However, the molecular weight is larger and the hydrotropic effect toward benzoic acid is greater. The presence of a second sulfonate group on the ring eliminates the salting-in effect toward benzoic acid and causes a slight degree of salting out to occur.

An aqueous sodium p-bromobenzenesulfonate solution should make an excellent medium for reactions involving the oxidation of compounds (capable of being hydrotropically dissolved) with strong oxidizing agents such as permanganate or dichromate, since the salt is very stable to oxidation itself.

The data for the solubility of benzoic acid in aqueous sodium o-xylenesulfonate solutions was tested in Setschenow's Equation (see page 6.)

$$\log \frac{S_o}{S} = KC .$$

This could be done only in an approximate manner since in this equation S and S_o are solubilities in weight units of non-electrolyte per liter of solution and C is the concentration of salt in mols per liter of solutions. It was impossible to express the solubility data in these terms, since no densities of the solutions were determined. However, as an approximation, the solubilities were expressed per 1000 grams of solution rather than per liter of solution. Straight lines were obtained for concentrations of sodium o-xylenesulfonate up to 1.3 molal by plotting solubility of benzoic acid at the three temperatures against molality of the salt on semi-log coordinates. The value of K was found to be -0.63 at each temperature.

Straight lines were also obtained by plotting the analogous data for sodium benzenesulfonate, sodium p-toluenesulfonate, and sodium m-xylenesulfonate. However, these straight lines did not extend into the dilute solutions, but resulted between concentrations of 1.6 - 2.6 molal sodium benzenesulfonate, 1.0 - 1.8 molal sodium p-toluenesulfonate, and 0.8 - 1.4 molal sodium m-xylenesulfonate. (see figure 12.).

FIGURE 11: SOLUBILITY OF BENZOIC ACID (BzOH) IN AQUEOUS SODIUM o-XYLENESULFONATE (NaXS) SOLUTIONS

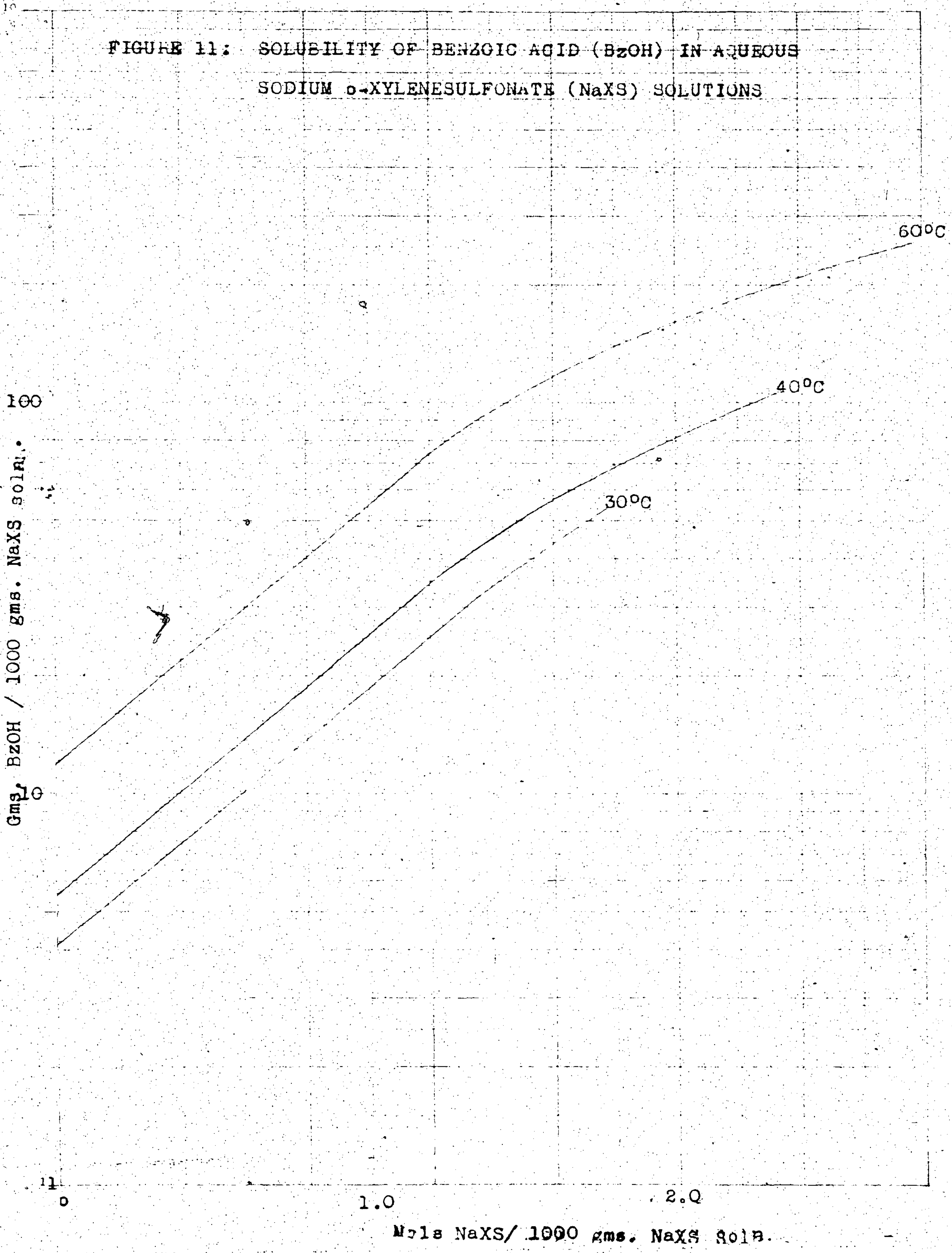
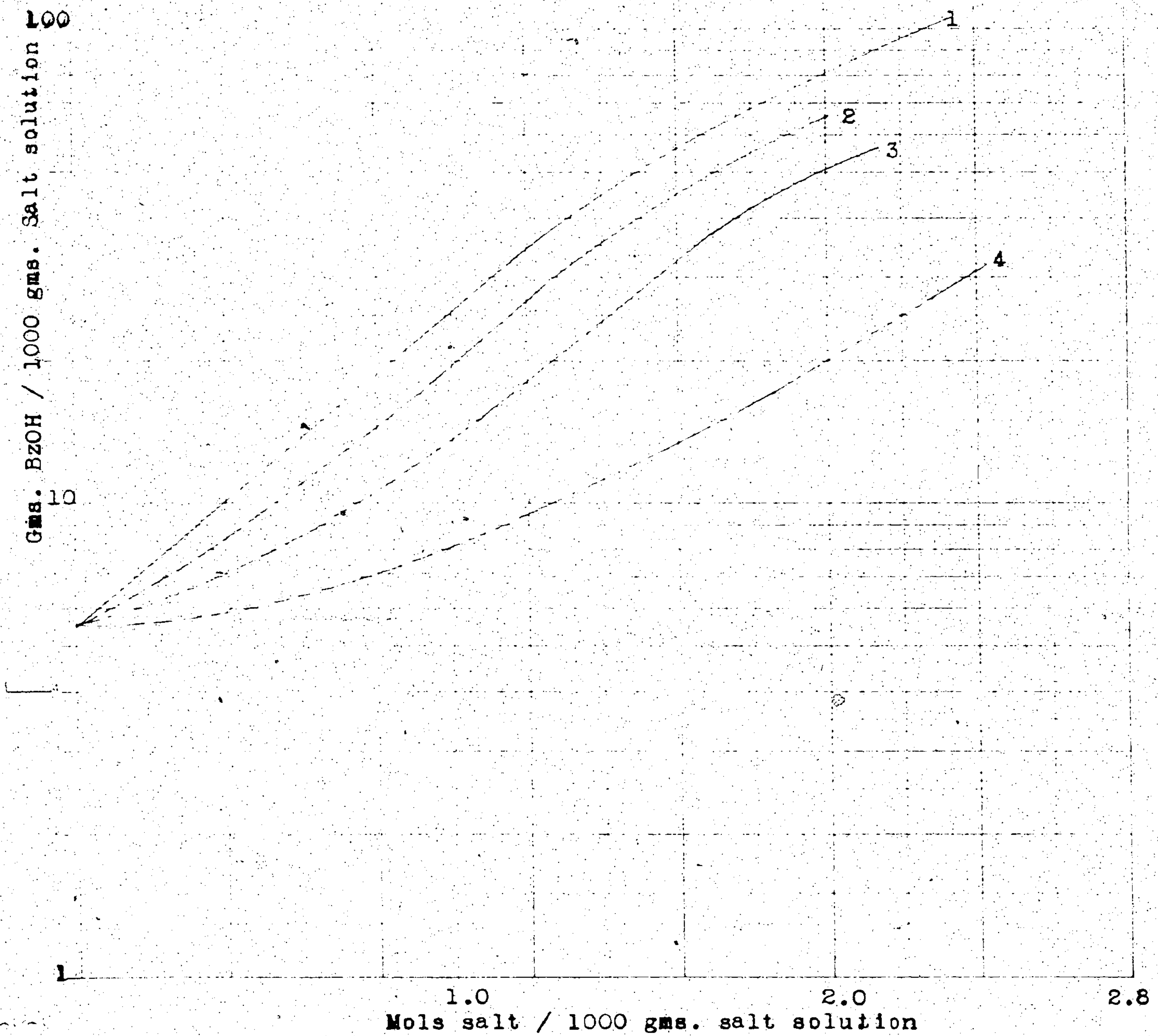


FIGURE 12: SOLUBILITY OF BENZOIC ACID (B_zOH) IN AQUEOUS HYDROTROPIC SALT SOLUTIONS AT 40°C.

1- SODIUM o-XYLENESULFONATE
2- SODIUM m-XYLENESULFONATE
3- SODIUM p-TOLUENESULFONATE
4- SODIUM BENZENESULFONATE



Bancroft (1) has stated that hydrotropic solvents may be compared to mixed liquid solvents in their action. The action of mixed liquid solvents is based on similarity in structure between one of the liquids, and the substance dissolved. The greater the percentage of this liquid present, the more the substance is dissolved. In the ideal case the solubility of the third component in the mixed solvent increases linearly with the weight fraction of solubilizing liquid in the mixed solvent. Thus, a plot of solubility of the third component versus composition of mixed solvent will yield a straight line.

This line of reasoning was applied to the system, water, benzoic acid, and sodium o-xylenesulfonate. The solubility data was first recalculated as solubility of benzoic acid in grams per 1000 grams of sodium o-xylenesulfonate solution, and weight percentage of sodium o-xylenesulfonate in the sodium o-xylenesulfonate solution. These were plotted as ordinate and abcissa, respectively. It was thought that there might arise a straight line which could be extended to the sodium o-xylenesulfonate axis and give a fictitious solubility of benzoic acid in pure sodium o-xylenesulfonate.

Plots of this data on rectangular coordinates and on semi-log coordinates are shown in figures 13 and 14. As shown, an exponential type of curve rather than a straight line is obtained on rectangular coordinates. It is interest-

FIGURE 13: SOLUBILITY OF BENZOIC ACID (BzOH) IN AQUEOUS SODIUM o-XYLENESULFONATE (NaXS) SOLUTIONS

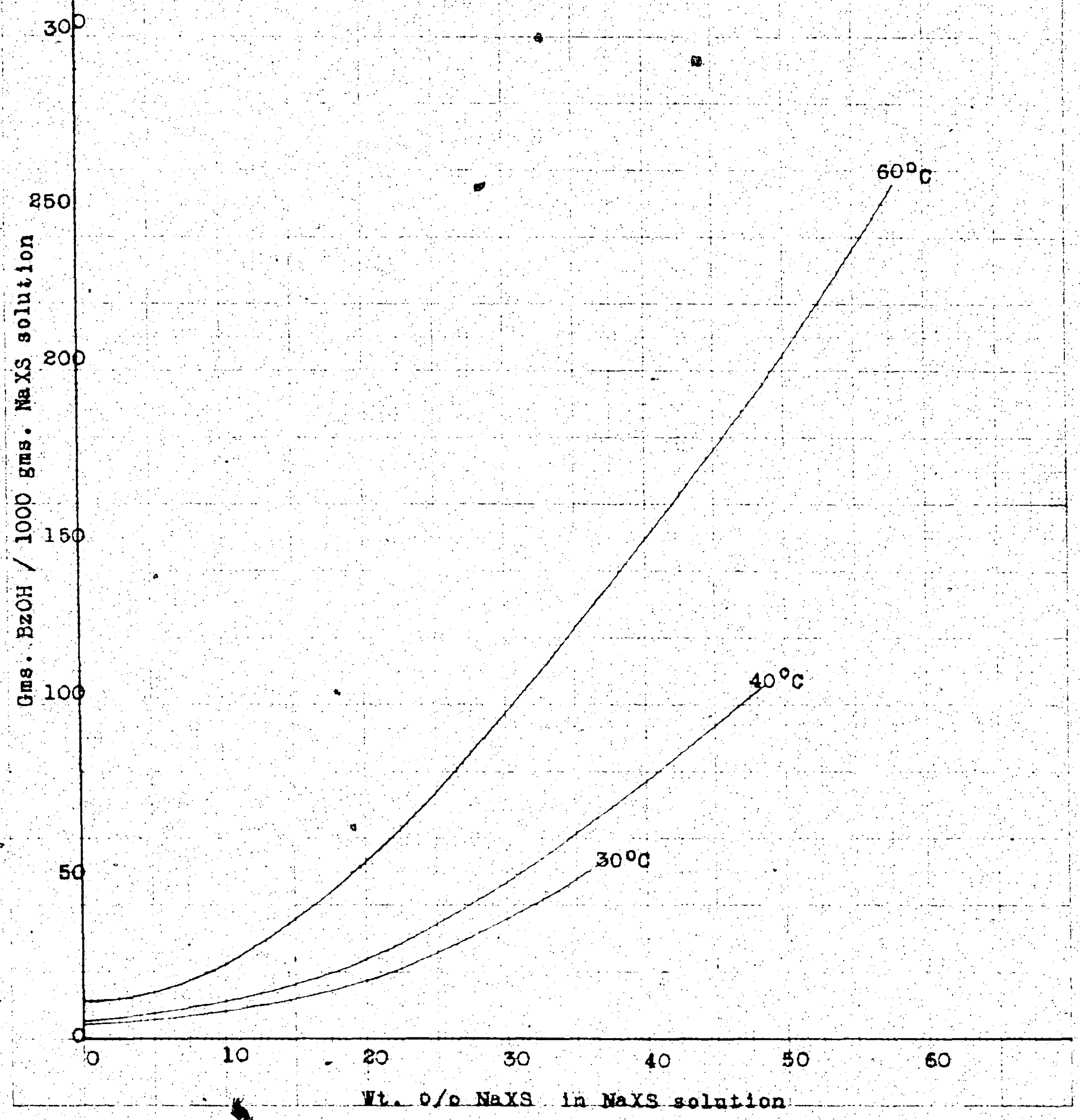
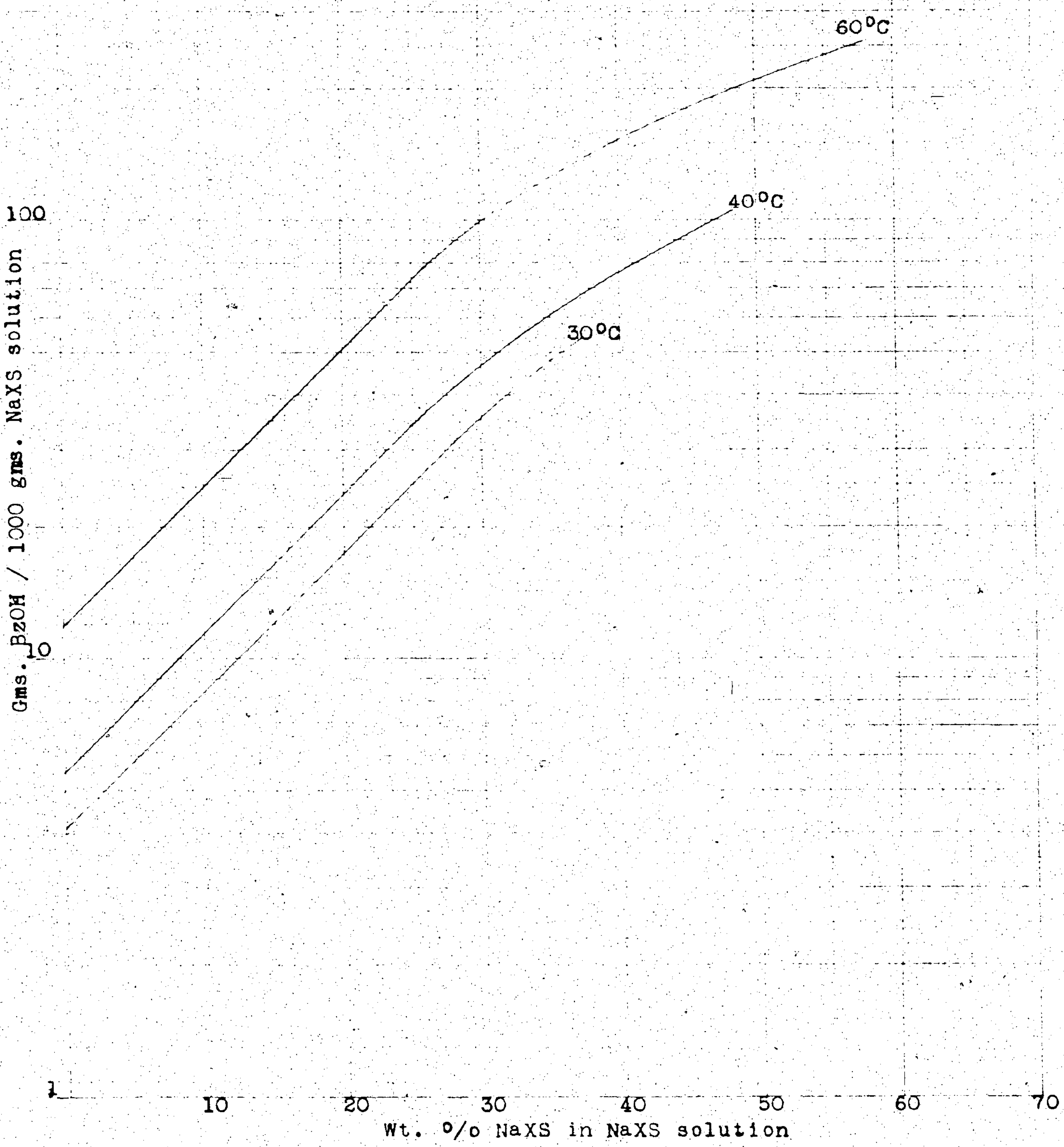


FIGURE 14: SOLUBILITY OF BENZOIC ACID (BzOH) IN AQUEOUS SODIUM o-XYLENEFULFONATE (NaXS) SOLUTIONS



ing to note that on the semi-log plot there is obtained a straight line at concentrations up to 15 percent by weight of sodium o-xylenesulfonate, and that the straight line portions for the three temperatures are parallel. Expressing this mathematically,

$$\frac{d \ln S_{BzOH}}{d\ C_{NaXS}} = K, \text{ or } \quad \frac{1}{S_{BzOH}} \ \frac{d\ S_{BzOH}}{d\ C_{NaXS}} = K.$$

This means that the rate of change of solubility of benzoic acid in sodium o-xylenesulfonate solution with the concentration of sodium o-xylenesulfonate solution is a linear function of the solubility of benzoic acid in sodium o-xylenesulfonate solution. The proportiohality constant, K, is independent of temperature.

The integrated form of this equation corresponds to Setschenow's equation (see page 6). However, the value of K is different, because the solubility of benzoic acid and concentration of sodium o-xylenesulfonate are expressed differently.

Following from the above line of reasoning thatthere might be a fictitious solubility of benzoic acid in sodium o-xylenesulfonate, it is logical to assume that the solubility of benzoic acid in aqueous sodium o-xylenesulfonate solutions is due to one of the three following reasons:

1) Similarity in structure of benzoic acid and sodium o-xylenesulfonate, alone.

2) A "salt effect" (see page 2) in addition to similarity in structure.

3) A "salt effect" alone.

Each of these will be considered individually. If similarity in structure alone is the cause of the solubilizing action, the ratio of grams of benzoic acid exclusive of the amount dissolved in the water to grams of sodium o-xylenesulfonate in the solution should be constant at all concentrations of sodium o-xylenesulfonate. In other words, this is considered to be an ideal case of a mixed liquid solvent.

If there is a salt effect in addition to the solubilizing effect due to similarity in structure, the above ratio would no longer be constant, but would be expected to increase with increased salt concentration. However, an indication of the solubilizing effect due to similarity in structure can be determined by extrapolating the curve to zero salt concentration, where the salt effect is zero.

If the solubility of benzoic acid in sodium o-xylenesulfonate solution is due only to a salt effect the extrapolation of the above curve should intersect the water axis at a ratio value of zero.

In figure 15 is shown a plot of this ratio versus mols of sodium o-xylenesulfonate per 1000 grams of water for the three temperatures. The curves at 30°, 40° and 60°C extrapolate to zero. It is therefore concluded that the solubility of benzoic acid in sodium o-xylenesulfonate solution is due solely to a salt effect.

The same type of curves are shown for solutions involving sodium benzenesulfonate, sodium p-toluenesulfonate, and sodium m-xylenesulfonate in figure 16. These curves are

FIGURE 15: RATIO OF BENZOIC ACID (BzOH) TO SODIUM o-XYLENESULFONATE (NaXS)

CORRECTED FOR BENZOIC ACID IN WATER PRESENT

- VERSUS -

MOLS SODIUM o-XYLENESULFONATE / 1000 GMS. H_2O

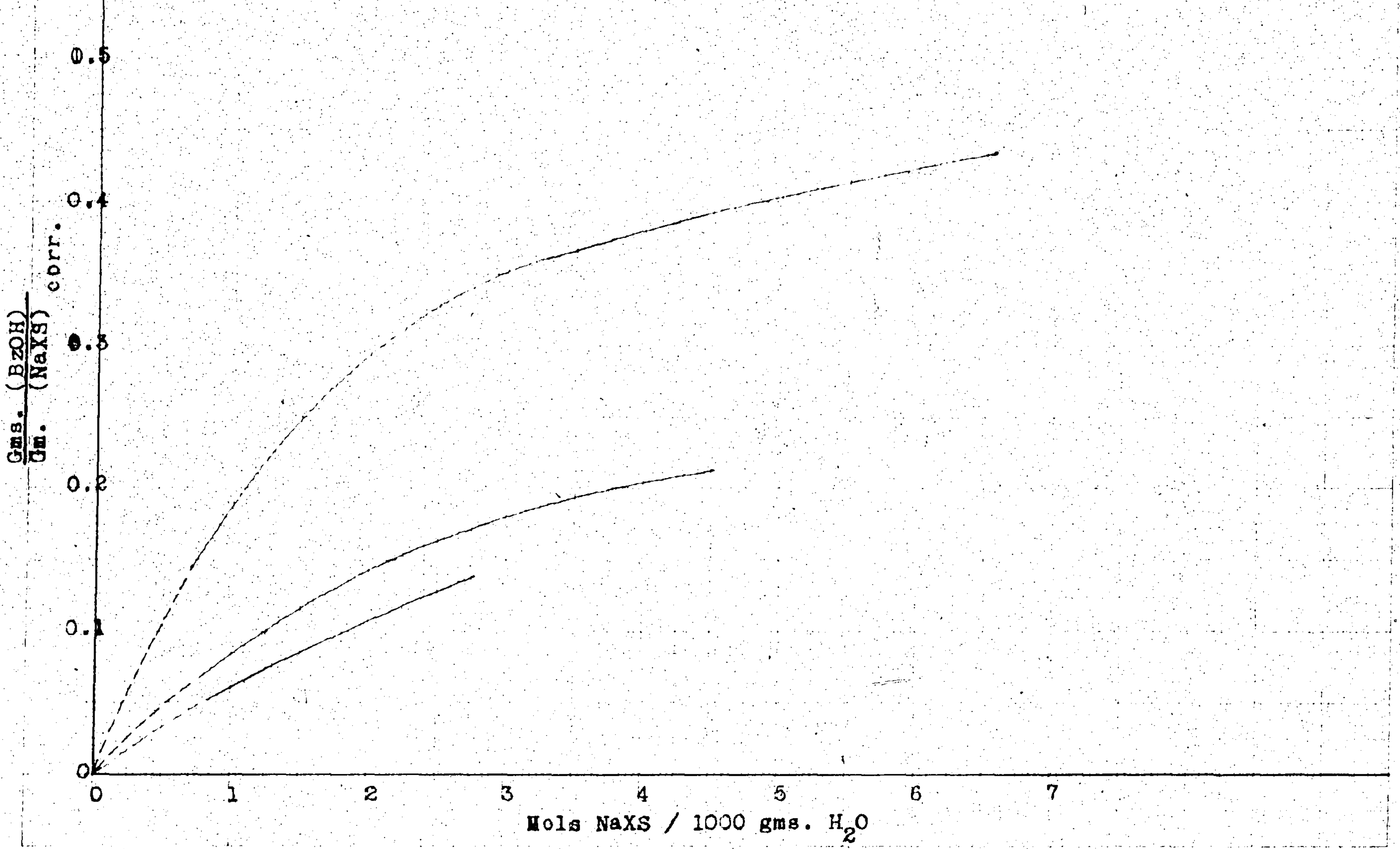


FIGURE 16: RATIO OF BENZOIC ACID (BzOH) TO HYDROTROPIC SALT CORRECTED FOR BENZOIC ACID IN WATER PRESENT AT 40°C.

- VERSUS -

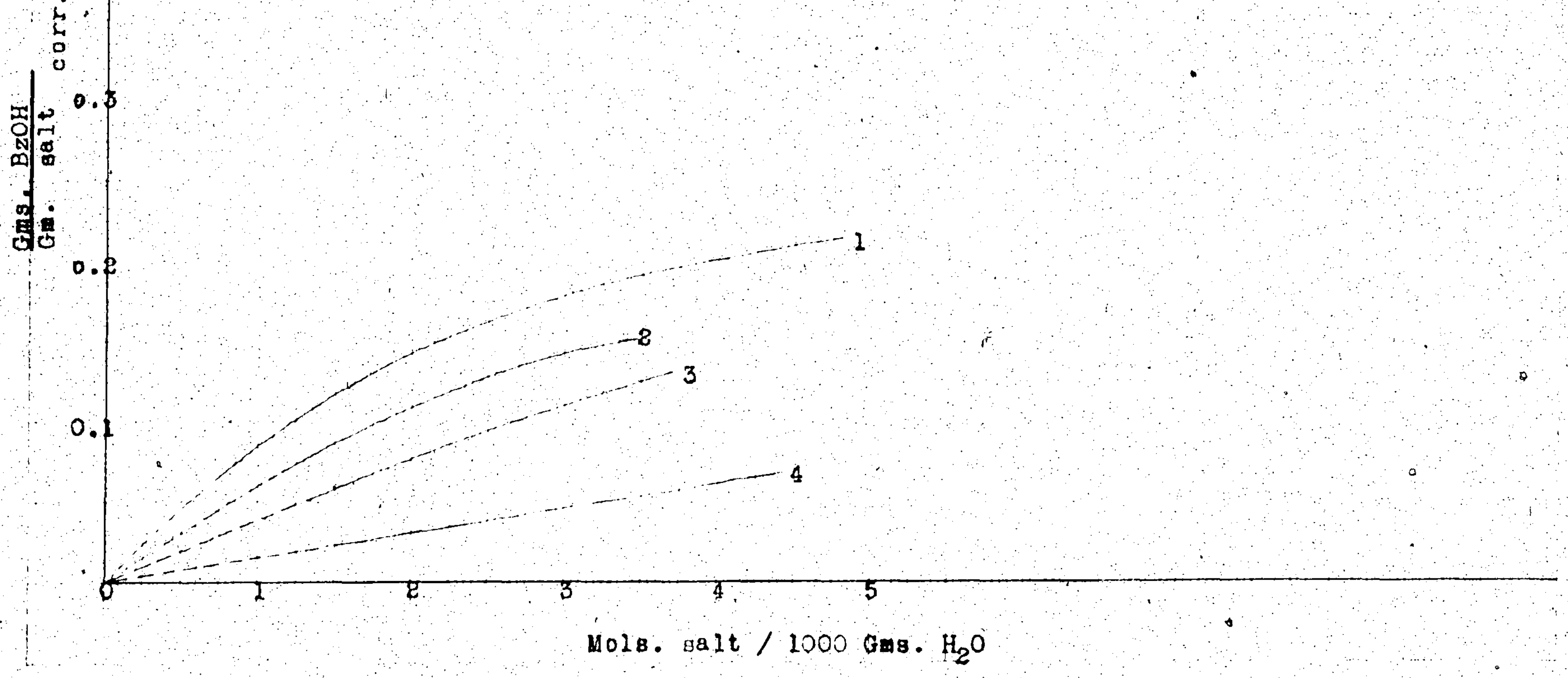
MOLS SALT / 1000 GMS. H_2O

1- SODIUM o-XYLENESULFONATE

2- SODIUM m-XYLENEFULFONATE

3- SODIUM p-TOLUENESULFONATE

4- SODIUM BENZENESULFONITE



also extrapolated to zero; thus indicating that the solvent action of these aqueous salt solutions toward benzoic acid is due only to a "salt effect".

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V APPENDIX

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Definitions of terms

BzOH = Benzoic acid.

Hydrotropic salts

NaXS = sodium o-xylenesulfonate
NamXS = sodium m-xylenesulfonate
NaBS = sodium benzenesulfonate
NaBDS = sodium m-benzenesulfonate
NaTS = sodium p-toluenesulfonate
NaCS = sodium p-cymenesulfonate
NaBrBS = sodium p-bromobenzenesulfonate
NaCin = sodium cinnamate

$$\text{Wt. \% BzOH} = \frac{\text{ml. NaOH} \times \text{Norm. NaOH} \times \frac{\text{mol.wt. BzOH}}{1000}}{\text{wt. of sample}} \times 100$$

$$\text{Wt. \% salt} = \frac{\text{wt. of dried salt}}{\text{wt. of sample}} \times 100$$

$$\text{Wt. \% } H_2O = 100 - (\text{wt. \% BzOH} + \text{wt. \% salt}).$$

$$\text{M.BzOH} = \frac{\text{Mols BzOH}}{\text{1000 gms. soln.}} = \frac{\text{wt. \% BzOH} \times 10}{\text{Mol. wt. BzOH}}$$

$$\text{M. salt} = \frac{\text{Mols salt}}{\text{1000 gms. soln}} = \frac{\text{wt. \% salt} \times 10}{\text{Mol. wt. salt}}$$

$$\text{M.}' \text{ BzOH} = \frac{\text{Mols BzOH}}{\text{1000 gms. } H_2O} = \frac{\text{M. BzOH}}{\text{wt. \% } H_2O}$$

$$\text{M.}' \text{ salt} = \frac{\text{Mols salt}}{\text{1000 gms. } H_2O} = \frac{\text{M. salt}}{\text{Wt. \% } H_2O}$$

$$\text{S. BzOH} - \frac{\text{Gms. BzOH}}{\text{1000 gms. NaXS soln.}} = \frac{\text{wt.\% BzOH x 1000}}{\text{100 - wt. \% BzOH}}$$

$$\begin{array}{l}\text{Wt. \% NaXS}\\ \text{in NaXS soln.}\end{array} = \frac{\text{wt.\% NaXS x 100}}{\text{100 - wt. \% BzOH}}$$

$$\text{Molality salt soln.} = \frac{\text{Mols NaXS}}{\text{1000 gms NaXS soln.}} =$$

$$\frac{\text{wt. \% salt}}{\text{Mol. wt. salt}} \text{ x } \frac{1000}{\text{100 - wt. \% BzOH}}$$

$$\left(\frac{\text{Gms. BzOH}}{\text{Gm. salt}}\right)_{\text{corr.}} = \frac{\text{wt. \% BzOH} - \frac{0.41}{99.51} \text{ x wt. \% } H_2O}{\text{Wt. \% salt}} \quad \text{at 30° C.}$$

$$= \frac{\text{wt. \% BzOH} - \frac{0.55}{99.45} \text{ x wt. \% } H_2O}{\text{Wt. \% salt}} \quad \text{at 40° C.}$$

$$= \frac{\text{wt. \% BzOH} - \frac{1.18}{98.82} \text{ x wt. \% } H_2O}{\text{Wt. \% salt}} \quad \text{at 60° C.}$$

TABLE 1 - Analysis of Saturated Solutions

A	Run Number		1			2	
B	Temperature		30°			30°	
C	Hydrotropic Salt		NaXS			NaXS	
D	Weight of weighing bottle	31.4518	31.5121	33.9365	31.4508	31.5115	33.9367
E	Weight plus sample	41.5656	38.2171	44.0270	37.6024	36.9567	39.7573
F	Weight of sample	10.1138	6.7050	10.0905	6.1516	5.4452	5.8206
G	Ml. of NaOH solution	18.31	12.02	18.26	16.70	15.00	15.78
H	Normality of NaOH solution	.0498	.0498	.0498	.0498	.0498	.0498
I	Percent BzOH	1.10	1.09	1.10	1.65	1.67	1.65
J	Weight of weighing bottle	32.0692	32.8764		31.5853	32.8734	
K	Weight plus sample	35.9744	38.1419		36.2256	38.6230	
L	Weight of sample	3.9052	5.2655		4.6403	5.7496	
M	Weight plus dried sample	32.6389	33.6442		32.4827	33.9856	
N	Weight of Dried sample	0.5677	0.7678		0.8974	1.1122	
O	Percent Salt	14.54	14.58		19.34	19.34	
P	Average percent BzOH		1.10			1.65	
Q	Average percent Salt		14.56			19.34	
R	Percent H_2O		84.34			79.01	
S	Saturated with		BzOH			BzOH	

Table 1 (Continued)

A		3			4			5	
B		30°			30°			30°	
C		NaXS			NaXS			NaXS	
D	31.4512	31.5117	33.9367	31.4507	31.5117	33.9364	31.5111	33.9368	31.4507
E	38.1943	36.3449	40.2497	35.8460	34.7861	38.2137	35.6714	37.2246	35.2323
F	6.7431	4.8332	6.3130	4.3953	3.2744	4.2773	4.1603	3.2878	3.7816
G	26.18	18.72	24.45	22.35	16.67	21.75	29.71	23.42	27.10
H	.0498	.0498	.0498	.0498	.0498	.0498	.0498	.0498	.0498
I	2.36	2.36	2.36	3.09	3.10	3.09	4.34	4.33	4.36
J	31.4511	33.9371		32.0690	31.5851		31.5111	33.9367	
K	37.0282	39.4433		38.2659	37.5040		35.6311	38.2493	
L	5.5771	5.5062		6.1969	5.9189		4.1200	4.3126	
M	32.9150	35.3807		33.7564	33.1929		32.8663	35.3552	
N	1.4639	1.4436		1.6874	1.6078		1.3552	1.4185	
O	26.25	26.22		27.23	27.17		32.89	32.89	
P		2.36			3.09			4.34	
Q		26.23			27.20			32.89	
R		71.41			69.71			62.77	
S		BzOH			BzOH			BzOH	

Table 1 (Continued)

A		6		7			8	
B		30°		30°			30°	
C		NaXS		NaXS			NaXS	
D	31.5851	32.8734	58.3407	58.2743	59.3632	31.8504	33.9360	31.6623
E	33.9074	36.4407	62.2620	62.3241	62.9666	37.3436	41.1234	39.1167
F	2.3223	3.5673	3.9213	4.0498	3.6034	5.4932	7.1874	7.4544
G	18.61	28.62	12.38	12.76	11.36	10.60	14.02	14.40
H	.0498	.0498	.1331	.1331	.1331	.0494	.0494	.0494
I	4.87	4.88	5.13	5.12	5.12	1.07	1.08	1.07
J	31.8509	31.6634	30.8466	32.8109		31.5846	32.8732	
K	36.1711	36.3135	35.3784	37.3318		37.1834	38.0923	
L	4.3202	4.6501	4.5318	4.5209		5.5988	5.2191	
M	33.4646	33.3996	32.4354	34.3970		33.2615	34.4364	
N	1.6137	1.7362	1.5888	1.5861		1.6769	1.5632	
O	37.35	37.34	35.05	35.08		29.95	29.95	
P		4.87		5.12			1.07	
Q		37.35		35.06			29.95	
R		57.78		59.82			68.98	
S		Both		Both			NaXS	

Table 1 (Continued)

A		9			10			11	
B		30°			30°			30°	
C		NaXS			NaXS			NaXS	
D	31.4484	31.5108	32.1986	31.4480	31.5104	32.1982	31.4480	31.5104	32.1977
E	37.4570	37.4781	37.2063	35.4981	35.2080	35.5523	34.7464	35.4930	35.2839
F	6.0086	5.9673	5.0077	4.0501	3.6976	3.3541	3.2984	3.9826	3.0862
G	25.56	25.37	21.30	21.90	19.94	18.10	21.80	26.37	20.37
H	.0494	.0494	.0494	.0494	.0494	.0494	.0494	.0494	.0494
I	2.36	2.36	2.36	2.99	2.99	2.99	3.66	3.67	3.66
J	31.8504	31.6628		32.0687	31.5839		31.8510	31.6632	
K	36.7824	36.3223		37.5310	37.5132		37.6056	36.8991	
L	4.9320	4.6595		5.4623	5.9293		5.7546	5,2359	
M	33.4103	33.1356		33.8402	33.5077		33.7650	33.4048	
N	1.5599	1.4728		1.7715	1.9238		1.9140	1.7416	
O	31.63	31.61		32.43	32.45		33.26	33.26	
P		2.36			2.99			3.66	
Q		31.62			32.44			33.26	
R		66.02			64.57			63.08	
S		NaXS			NaXS			NaXS	

Table 1 (Continued)

A		12		13			14	
B		30°		40°			40°	
C		NaXS		NaXS			NaXS	
D			31.8504	31.5106	33.9362	31.8503	31.5108	33.9363
E			37.2512	36.2791	40.0938	37.0605	35.9293	38.5746
F			5.4008	4.7685	6.1576	5.2102	4.4165	4.6383
G			12.17	10.77	13.93	20.58	17.47	18.55
H			.0500	.0500	.0500	.0500	.0500	.0500
I		0.00	1.38	1.38	1.38	2.41	2.41	2.44
J	31.6630	32.8730	32.0687	31.5843		32.8730	31.6626	
K	37.7671	37.3571	37.3833	36.7208		37.8913	37.7544	
L	6.1041	4.4841	5.3146	5.1365		5.0183	6.0918	
M	33.4169	34.1630	32.7873	32.2795		33.8778	32.8822	
N	1.7539	1.2900	0.7186	0.6952		1.0048	1.2196	
O	28.73	28.77	13.52	13.53		20.02	20.02	
P		0.00		1.38			2.41	
Q		28.75		13.52			20.02	
R		71.25		85.20			77.57	
S		NaXS		BzOH			BzOH	

Table 1 (Continued)

A		15			16	17	
B		40°			40°	40°	
C		NaXS			NaXS	NaXS	
D	31.8505	31.5577	33.9365	31.8507	31.5579	31.8506	33.9361
E	35.8828	35.3480	37.4820	35.0686	34.6505	35.0533	36.7006
F	4.0323	3.7903	3.5455	3.2179	3.0926	3.2027	2.7645
G	21.75	20.46	19.25	24.93	23.90	29.38	25.25
H	.0500	.0500	.0500	.0500	.0500	.0500	.0500
I	3.29	3.30	3.31	4.73	4.72	5.60	5.58
J	32.0690	31.5846		32.8732	31.6628	32.0689	31.5846
K	37.3002	37.3205		38.2424	37.5134	37.0684	36.2556
L	5.2312	5.7359		5.3692	5.8506	4.9995	4.6710
M	33.3282	33.9649		34.4500	33.3800	33.6928	33.1019
N	1.2592	1.3803		1.5768	1.7172	1.6239	1.5137
O	24.06	24.06		29.37	29.35	32.48	32.48
P		3.30			4.73		5.59
Q		24.06			29.36		32.48
R		72.64			65.91		61.93
S		BzOH			BzOH		BzOH

Table 1 (Continued)

A		18		19			20
B		40°		40°			40°
C		NaXS		NaXS			NaXS
D	31.8505	31.5574	31.8506	32.0687	31.5850		
E	35.8485	35.1844	35.8846	35.8941	35.7092		
F	3.9980	3.6270	4.0340	3.8254	4.1242		
G	22.25	20.22	31.06	29.53	31.85		
H	.1024	.1024	.0963	.0963	.0963		
I	6.96	6.97	8.51	8.53	8.53		0.00
J	32.8733	31.6628	21.5578	33.9317		32.8734	31.6628
K	38.0100	37.1513	37.2954	39.9640		38.3070	36.8050
L	5.1367	5.4885	5.7376	6.0274		5.4336	5.1422
M	34.7503	33.6683	34.0515	36.5553		35.0514	33.7246
N	1.8770	2.0055	2.4937	2.6191		2.1770	2.0618
O	36.54	36.54	43.47	43.45		40.08	40.10
P		6.97		8.53			0.00
Q		36.54		43.46			40.09
R		56.49		48.01			59.91
S		BzOH		NaXS			NaXS

Table 1 (Continued)

A		21			22			23
B		40°			40°			40°
C		NaXS			NaXS			NaXS
D	31.8506	32.8734	31.6628	31.5583	33.9368	30.5336	31.5581	30.5331
E	38.0993	39.2536	38.6784	36.6523	38.8723	35.7392	36.3546	34.9594
F	6.2487	6.3802	7.0156	5.0940	3.9355	5.2056	4.7965	4.4263
G	15.17	15.62	17.12	25.80	19.96	26.43	26.03	23.92
H	.0963	.0963	.0963	.0963	.0963	.0963	.0963	.0963
I	2.68	2.70	2.69	5.60	5.60	5.61	6.00	5.98
J	32.0689	31.5847		31.8513	31.6632			32.0690
K	37.8683	36.9190		37.5178	38.4464			37.9500
L	5.7994	5.3343		5.6665	6.7832			5.8810
M	34.4953	33.8183		34.2819	34.5738			34.5927
N	2.4264	2.2336		2.4306	2.9106			2.5237
O	41.84	41.87		43.89	42.91			43.01
P		2.69			5.60			5.99
Q		41.85			42.90			43.01
R		55.46			51.50			51.00
S		NaXS			NaXS			NaXS

Table 1 (Continued)

A		24		25			26
B		40°		40°			40°
C		NaXS		NaXS			NaXS
D	31.5585	33.9368	31.8507	30.5319	32.7788	31.8506	30.5316
E	35.8490	36.8780	35.1293	33.7154	36.3265	34.7653	34.2218
F	4.2905	2.9412	3.2786	3.1835	3.5477	2.9147	3.6902
G	32.46	22.18	30.80	29.85	33.31	28.02	35.46
H	.0963	.0963	.0813	.0813	.0813	.0813	.0813
I	8.36	8.34	9.33	9.31	9.32	9.55	9.54
J	32.0694	31.5852	32.0696	31.5846			32.0691
K	38.3917	37.9896	37.9821	36.8231			37.3203
L	6.3223	6.4044	5.9125	5.2385			5.2512
M	34.8117	34.3621	34.6307	33.8541			34.3696
N	1.7423	1.7769	2.5611	2.2695			2.3005
O	43.38	43.36	43.31	43.32			43.80
P		8.35		9.32			9.54
Q		43.37		43.31			43.80
R		48.28		47.37			46.66
S		NaXS		BzOH			Both

Table 1 (Continued)

A		27			28			29
B		50°			60°			60°
C		NaXS			NaXS			NaXS
D	31.8503	32.8627	31.5785	31.8508	30.5316	32.8629		
E	34.8782	35.9791	33.8809	33.8295	32.6164	34.8456		
F	3.0276	3.1164	2.3024	1.9787	2.0848	1.9827		
G	35.70	36.71	27.16	39.62	41.72	39.70		
H	.0813	.0813	.0813	.0821	.0821	.0821		
I	11.71	11.69	11.71	20.06	20.05	20.06		0.00
J	32.0691	31.5842		32.0690	31.5840		31.5784	33.8691
K	37.3548	37.6089		36.6620	34.8949		36.3904	38.7961
L	5.2857	6.0247		4.5930	3.3109		4.8120	4.9270
M	34.2478	34.0683		34.1774	33.1053		33.8176	35.1622
N	2.1787	2.4841		2.1064	1.5213		2.2392	2.2931
O	41.2 2	41.22		45.91	45.92		46.53	46.53
P		11.70			20.06			0.00
Q		41.22			45.92			46.53
R		47.08			34.02			53.47
S		BzOH			BzOH			NaXS

Table 1 (Continued)

A		30		31		32	
B		60°		60°		60°	
C		NaXS		NaXS		NaXS	
D	30.5316	32.8622	58.3418	58.0417	58.3405	60.6864	58.0407
E	32.9551	34.9450	62.7778	62.7608	62.4594	64.6683	62.0708
F	2.4235	2.0828	4.4360	4.7190	4.1189	3.9819	4.0301
G	24.98	21.49	32.48	34.60	16.26	15.70	15.86
H	.0821	.0821	.1003	.1003	.1003	.1003	.1003
I	10.33	10.34	8.97	8.98	4.84	4.83	4.82
J	32.0688	31.5859	31.8498	30.5310	31.5785	31.5841	
K	37.5625	35.2307	35.8989	35.8853	36.5404	37.1385	
L	5.4937	3.6468	4.0491	5.3543	4.9619	5.5544	
M	33.7244	32.6837	32.9503	31.9860	32.5086	32.6253	
N	1.6556	1.0998	1.1005	1.4550	0.9301	1.0412	
O	30.14	30.16	27.18	27.17	18.74	18.75	
P		10.34		8.98		4.83	
Q		30.15		27.17		18.74	
R		59.51		63.85		76.43	
S		BzOH		BzOH		BzOH	

Table 1 (Continued)

A		33			34			35	
B		60°			60°			60°	
C		NaXS			NaXS			NaXS	
D	58.3421	60.6869	58.0414	60.6868	58.0409		58.3408	60.6863	58.0410
E	68.0974	68.8265	67.9103	65.0265	62.7306		65.4060	67.7363	64.9065
F	9.7553	8.1396	9.8689	4.3397	4.6897		7.0652	7.0500	6.8655
G	9.50	7.79	9.56	47.03	50.86		16.20	16.32	15.70
H	.1003	.1003	.1003	.1003	.1003		.1003	.1003	.1003
I	1.19	1.17	1.19	13.27	13.28		2.81	2.83	2.81
J				30.6632	31.1036		31.8509	30.5317	
K				36.0831	36.1643		36.8018	35.8317	
L				5.4199	5.0607		4.9509	5.3000	
M				32.5691	32.8828		32.4660	31.1911	
N				1.9059	1.7792		0.6151	0.6594	
O		0.00		35.16	35.15		12.43	12.44	
P		1.18			13.28			2.81	
Q		0.00			35.15			12.43	
R		98.82			51.57			84.76	
S		BzOH			BzOH			BzOH	

Table 1 (Continued)

A		36			37			38	
B		60°			60°			60°	
C		NaXS			NaXS			NaXS	
D	58.3411	60.6865	58.0407	58.3418	60.6875	58.0414	58.3414	60.6868	58.0408
E	63.3114	65.8422	62.8811	63.9892	65.8729	63.3310	61.8101	64.4120	61.7970
F	4.9703	5.1557	4.8404	5.6474	5.1854	5.2896	3.4687	3.7252	3.7562
G	47.03	48.98	45.94	23.21	21.31	21.77	38.33	41.05	41.41
H	.1003	.1003	.1003	.1010	.1010	.1010	.1010	.1010	.1010
I	11.67	11.69	11.68	5.07	5.07	5.09	13.57	13.54	13.55
J	31.5841	32.8621		32.0207	30.6791		30.6624	30.5317	
K	37.7523	38.3182		38.0888	36.0652		36.2276	36.7521	
L	6.1682	5.4561		6.0681	5.3861		5.5652	6.2204	
M	34.5052	35.4473		34.8971	33.2327		32.6467	32.7479	
N	2.9211	2.5852		2.8764	2.5536		1.9843	2.2162	
O	47.34	47.37		47.40	47.40		35.66	35.63	
P		11.68			5.07			13.55	
Q		47.36			47.40			35.64	
R		40.96			47.53			50.81	
S		NaXS			NaXS			BzOH	

Table 1 (Continued)

A	39			40		41
B	60°			60°		60°
C	NaXS			NaXS		NaXS
D	60.6870	58.0410	58.3411	60.6864	58.3411	60.6864
E	63.2371	60.6908	61.0498	63.0587	60.6000	63.0747
F	2.5501	2.6498	2.7087	2.3723	2.2589	2.3883
G	39.54	41.07	40.80	35.76	32.05	33.90
H	.1010	.1010	.1108	.1108	.1108	.1108
I	19.05	19.04	20.38	20.40	19.20	19.20
J	31.8504	31.1028	31.6628	30.6801	32.0208	32.7785
K	37.0945	37.0689	36.9718	36.5189	37.7824	37.7091
L	5.2441	5.9661	5.3090	5.8388	5.7616	4.9306
M	34.1985	33.7717	34.1035	33.3622	34.5899	34.9786
N	2.3481	2.6689	2.4407	2.6821	2.5691	2.2001
O	44.77	44.75	45.97	46.03	44.57	44.62
P	19.05			20.39		19.20
Q	44.76			46.00		44.60
R	36.19			33.61		36.20
S	BzOH			Both		BzOH

Table 1 (Continued)

A		42		43		44	
B		60°		60°		60°	
C		NaXS		NaXS		NaXS	
D	58.3417	60.6865	60.6858	58.0395	58.3400	60.6861	58.0395
E	60.7049	62.6106	62.8599	60.2298	60.5240	62.8335	60.3122
F	2.3632	1.9241	2.1741	2.1903	2.1840	2.1474	2.2727
G	33.50	27.20	31.34	31.57	31.41	30.90	32.72
H	.1108	.1108	.1108	.1108	.1114	.1114	.1114
I	19.18	19.12	19.65	19.64	19.60	19.61	19.62
J	31.5839	31.4473	30.6614	30.5311	31.8501	31.1019	
K	36.3580	36.6457	36.3552	36.1954	37.5477	36.1589	
L	4.7741	5.1984	5.6938	5.6643	5.6976	5.0570	
M	33.7220	33.7771	33.2204	33.0748	34.4225	33.3815	
N	2.1381	2.3298	2.5590	2.5437	2.5724	2.2796	
O	44.78	44.82	44.94	44.91	45.13	45.07	
P		19.15		19.65		19.61	
Q		44.80		44.92		45.10	
R		36.05		35.43		35.29	
S		BzOH		BzOH		BzOH	

Table 1 (Continued)

A		45		46			47
B		60°		60°			60°
C		NaXS		NaXS			NaXS
D	58.3401	60.6858	58.3406	60.6864	58.0404	58.3410	58.0402
E	60.2756	62.6262	60.0412	62.1431	60.1465	60.9436	61.9463
F	1.9355	1.9404	1.7006	1.4557	2.1061	2.6026	3.9061
G	28.26	28.34	25.02	21.43	30.92	17.74	26.60
H	.1114	.1114	.1114	.1114	.1114	.1114	.1114
I	19.85	19.86	19.99	20.02	19.97	9.26	9.24
J	30.6798	31.6624	31.5838	32.9571		31.8490	31.1015
K	35.4515	36.5627	34.2424	35.7715		35.5690	36.7876
L	4.7717	4.9003	2.6586	2.8144		3.7200	5.6861
M	32.8645	33.9044	32.8104	34.2571		33.6108	33.7895
N	2.1847	2.2420	1.2269	1.3000		1.7618	2.6880
O	45.78	45.75	46.14	46.20		47.35	47.28
P		19.86		19.99			9.25
Q		45.76		46.17			47.31
R		34.38		33.84			43.44
S		BzOH		NaXS			NaXS

Table 1 (Continued)

A		48		49		50
B		60°		60°		60°
C		NaXS		NaXS		NaXS
D	58.3404	58.0397	58.3404	58.0402	58.3412	58.0403
E	60.2326	60.0130	60.2424	59.9579	60.2125	60.1369
F	1.8922	1.9733	1.9020	1.9177	1.8713	2.0966
G	21.80	22.70	21.20	21.46	15.44	17.27
H	.1114	.1114	.0980	.0980	.1109	.1109
I	15.65	15.62	13.37	13.39	11.18	11.16
J	30.6616	30.5313	30.6614	30.5312	32.0203	32.9573
K	35.3670	35.3970	36.4802	36.2920	37.3705	37.0504
L	4.7054	4.8657	5.8188	5.7608	5.3502	4.0931
M	32.8696	32.8111	33.3987	33.2473	34.5677	34.9020
N	2.2080	2.2798	2.7373	2.7161	2.5474	1.9447
O	46.91	46.86	47.13	47.26	47.59	47.52
P		15.64		13.38		11.17
Q		46.88		47.20		47.55
R		37.48		39.42		41.28
S		NaXS		NaXS		NaXS

Table 1 (Continued)

A		51			52			53	
B		40°			40°			40°	
C		Nam·XS			Nam·XS			NaTS	
D	58.3411	60.6868	58.0410	58.3403	60.6856	58.0396	31.5839	30.5311	33.8679
E	61.4881	63.2719	60.9989	60.8455	63.4208	61.1238	34.1242	32.9135	37.1165
F	3.1470	2.5851	2.9479	2.5052	2.7352	3.0842	2.5403	2.3824	3.2486
G	14.41	11.82	13.49	13.73	15.00	16.94	9.30	8.73	11.98
H	.1102	.1102	.1102	.1102	.1102	.1102	.1102	.1102	.1102
I	6.16	6.15	6.16	7.37	7.38	7.39	4.93	4.93	4.96
J	30.6797	31.6629		32.0201	32.9571		30.6610	31.1016	
K	36.4383	37.1253		35.8442	37.2845		36.6623	36.1198	
L	5.7586	5.4624		3.8241	4.3274		6.0013	5.0182	
M	32.9295	33.7967		33.7300	34.8931		32.7902	32.8821	
N	2.2498	2.1338		1.7099	1.9360		2.1292	1.7805	
O	39.06	39.06		44.70	44.74		35.48	35.48	
P		6.16			7.38			4.94	
Q		39.06			44.72			35.48	
R		54.78			47.90			59.58	
S		BzOH			BzOH			BzOH	

Table 1 (Continued)

A		54		55			56
B		40°		40°			40°
C		NaCin		NaBDS			NaBDS
D	58.3404	58.0396	58.3415	60.6870	58.0406	58.3405	58.0391
E	63.0218	62.3397	61.7589	65.6207	62.4842	65.1860	62.4470
F	4.7812	4.3001	3.4174	4.9337	4.4436	6.8455	4.4079
G	1.00	0.90	0.67	0.83	0.78	1.72	1.10
H	.1102	.1102	.1102	.1102	.1102	.1102	.1102
I	0.28	0.28	0.26	0.23	0.24	0.34	0.34
J	30.5315	33.8682	30.6807	32.9581		32.1885	33.8680
K	36.5015	38.6994	35.6261	38.2482		38.2813	40.5451
L	5.9700	4.8312	4.9454	5.2901		6.0928	6.6771
M	31.0722	34.3045	32.4815	34.8841		34.5921	36.5007
N	0.5407	0.4363	1.8008	1.9260		2.4036	2.6327
O	9.06	9.04	36.41	36.41		39.45	39.43
P		0.28		0.24			0.34
Q		9.05		36.41			39.44
R		90.67		63.35			60.22
S		Both		BzOH			BzOH

Table 1 (Continued)

A		57		58			59	
B		40°		40°			40°	
C		NaBrBS		NaBrBS			NaBS	
D	60.6865	58.0396	30.6797	58.3411	32.9576	58.3396	60.6860	58.0394
E	65.8995	62.8933	34.9824	62.3007	37.5872	61.9754	64.2721	60.5754
F	5.2130	4.8587	4.3027	3.9596	4.6296	3.6358	3.5861	2.5360
G	6.46	6.05	16.59	15.33	17.81	7.86	7.71	5.49
H	.1180	.1180	.1180	.1180	.1180	.1180	.1180	.1180
I	1.18	1.18	4.28	4.30	4.26	3.11	3.10	3.12
J	31.2688	32.3901	32.1889	33.8687		30.6794	32.9574	
K	36.2085	37.1727	37.6759	38.4875		33.4864	37.4899	
L	4.9397	4.8826	5.4870	4.6188		2.8070	4.5321	
M	32.0348	33.0481	33.9722	35.3702		31.8647	34.8701	
N	0.7660	0.7580	1.7833	1.5015		1.1853	1.9127	
O	15.51	15.53	32.49	32.51		42.22	42.19	
P		1.18		4.28			3.11	
Q		15.52		32.50			42.20	
R		83.40		63.22			54.69	
S		BzOH		BzOH			BzOH	

Table 1 (Continued)

A		60			61			62	
B		40°			40°			40°	
C		NaBrBS			NaBrBS			NaBS	
D	58.3395	60.6856	58.0396	58.3401	60.6857	58.0401	58.3409	60.6857	58.0406
E	61.8386	64.8397	62.0836	61.1403	64.3042	62.1251	63.1367	66.1223	62.6464
F	3.4991	4.1541	4.0440	2.8002	3.6185	4.0850	4.7958	5.4366	4.6058
G	8.94	10.56	10.28	11.98	15.49	17.49	5.46	6.11	5.15
H	.1180	.1180	.1180	.1180	.1180	.1180	.1180	.1180	.1180
I	2.70	2.68	2.68	4.78	4.79	4.79	1.64	1.62	1.62
J	30.6615	31.1019		30.7048	32.7844		32.0202	31.6632	
K	35.8494	36.3019		35.8566	37.8018		38.3461	36.4410	
L	5.1879	5.2000		5.1518	5.0174		6.3259	4.7778	
M	31.9555	32.3998		32.5074	34.5398		34.0518	33.1980	
N	1.2940	1.2979		1.8026	1.7554		2.0316	1.5348	
O	24.95	24.96		35.00	34.98		32.11	32.12	
P		2.68			4.79			1.62	
Q		24.95			34.99			32.11	
R		72.37			60.22			66.27	
S		BzOH			BzOH			BzOH	

Table 1 (Continued)

A		63			64			65
B		40°			40°			40°
C		NaCS			NaBS			NaCS
D	58.3412	60.6868	58.0405	58.3409	60.6865	58.0402	58.3408	60.6861
E	62.6665	64.8663	61.9400	63.8161	66.6410	62.9709	60.6214	63.4347
F	4.3257	4.1795	3.8995	5.4752	5.9545	4.9307	2.2806	2.7486
G	14.70	14.24	13.31	3.46	3.79	3.14	11.95	14.39
H	.1180	.1180	.1180	.1180	.1180	.1180	.1180	.1180
I	4.90	4.91	4.92	0.91	0.92	0.92	7.55	7.54
J	31.6272	31.3849		31.2688	31.1024		30.6620	32.2897
K	36.9277	36.7486		36.6539	36.8464		36.2581	37.6633
L	5.3005	5.3637		5.3851	5.7440		5.5961	5.3736
M	33.1508	32.9263		32.4026	32.3125		32.9362	34.4745
N	1.5236	1.5414		1.1338	1.2101		2.2742	2.1848
O	28.74	28.74		21.06	21.07		40.64	40.65
P		4.91			0.92			7.54
Q		28.74			21.05			40.64
R		66.35			78.02			51.82
S		BzOH			BzOH			BzOH

Table 1 (Continued)

A		66			67			68	
B		40°			40°			40°	
C		NaCS			NaCS			NaCS	
D	58.3406	60.6865	58.047	58.3405	60.6859	58.0404	58.3413	60.6860	58.0404
E	62.0528	64.2035	61.6186	63.2603	66.0579	62.7724	63.4845	65.5776	62.4187
F	3.7122	3.5270	3.5779	4.9198	5.3720	4.7320	5.1432	4.8916	4.3783
G	29.72	28.18	28.72	14.31	15.60	13.81	7.66	7.27	6.51
H	.1180	.1180	.1180	.1180	.1180	.1180	.1180	.1180	.1180
I	11.54	11.52	11.56	4.19	4.20	4.20	2.15	2.14	2.14
J		32.9508		30.6799	33.8684		32.0203	31.1024	
K		37.6340		35.3508	38.8015		36.6100	35.3613	
L		4.6832		4.6709	4.9331		4.5897	4.2589	
M		35.4371		31.8590	35.1166		32.6982	31.7324	
N		2.4863		1.1793	1.2482		0.6779	0.6300	
O		53.10		25.25	25.30		14.76	14.76	
P		11.54			4.20			2.14	
Q		53.10			25.27			14.77	
R		35.36			70.53			83.09	
S		BzOH			BzOH			BzOH	

Table 1 (Continued)

A		69			70			71	
B		40°			40°			40°	
C		NaCS			Nam·XS			NaTS	
D	58.3414	60.6864	58.0413	58.3404	60.6852	58.0394	58.3412	60.6865	58.0404
E	63.2265	66.4047	63.1528	63.9510	66.6617	63.7650	64.2928	66.7914	64.4216
F	4.8851	5.7183	5.1115	5.6106	5.9765	5.7256	5.9516	6.1049	6.3812
G	3.57	4.19	3.73	6.05	6.46	6.19	5.39	5.56	5.30
H	.1180	.1180	.1180	.1328	.1328	.1328	.1328	.1328	.1328
I	1.05	1.06	.105	1.75	1.75	1.75	1.47	1.48	1.47
J	31.2687	31.6637		31.4073	32.6164		30.5470	31.9273	
K	35.5653	36.9855		37.1017	38.0467		36.0253	36.9655	
L	4.2966	5.3218		5.6944	5.4303		5.4783	5.0382	
M	31.6222	32.1003		32.4994	33.6581		31.6602	32.9514	
N	0.3535	0.4366		1.0921	1.0417		1.1132	1.0241	
O	8.23	8.21		19.18	19.18		20.32	20.32	
P		1.05			1.75			1.47	
Q		8.22			19.18			20.32	
R		90.73			79.07			78.21	
S		BzOH			BzOH			BzOH	

Table 1 (Continued)

A		72		73			74	
B		40°		40°			40°	
C		Nam·XS		NaTS			Nam·XS	
D	60.6859	58.0401	58.3408	60.6861	58.0405	58.3413	60.6861	58.0404
E	65.9229	62.9211	63.9475	65.9732	64.6154	62.4350	65.2126	62.9687
F	5.2370	4.8810	5.6067	5.2871	6.5749	4.0937	4.5265	4.9283
G	10.12	9.42	7.72	7.29	9.05	10.66	11.72	12.76
H	.1328	.1328	.1328	.1328	.1328	.1328	.1328	.1328
I	3.13	3.13	2.23	2.24	2.23	4.22	4.20	4.20
J	32.1889	30.2853	30.7057	32.9578		30.1653	32.8106	
K	37.1891	35.7853	36.3917	38.3178		36.3476	38.8475	
L	5.002	5.4990	5.6860	5.3600		6.1823	6.0369	
M	33.5194	31.7488	32.1713	34.3395		32.1126	34.7116	
N	1.3305	1.4635	1.4656	1.3817		1.9473	1.9010	
O	26.61	26.66	25.78	25.78		31.49	31.49	
P		3.13		2.23			4.20	
Q		26.63		25.78			31.49	
R		70.24		71.99			64.31	
S		BzOH		BzOH			BzOH	

Table 1 (Continued)

A		75			76			77	
B		40°			40°			40°	
C		NaTS			NaTS			NaTS	
D	58.3416	60.6864	58.0408	58.3408	60.6853	58.0394	58.3418	58.2750	59.3624
E	63.1510	66.1798	63.2407	63.1426	64.6955	62.2126	63.0219	61.9582	63.6177
F	4.8094	5.4934	5.1999	4.8018	4.0102	4.1732	4.6801	3.6832	4.2553
G	10.75	12.32	11.62	13.82	11.57	12.00	15.41	12.06	13.95
H	.1328	.1328	.1328	.1328	.1328	.1328	.1328	.1328	.1328
I	3.63	3.64	3.63	4.67	4.68	4.67	5.34	5.31	5.32
J	31.6409	31.0623		32.2108	33.1732		30.7045	32.9573	
K	37.3370	36.4342		37.3871	38.9242		36.4607	37.7171	
L	5.6961	5.3719		5.1763	5.7510		5.7562	4.7598	
M	33.4533	32.7713		34.1212	35.2955		32.9718	34.8336	
N	1.8124	1.7090		1.9104	2.1223		2.2673	1.8763	
O	31.82	31.81		36.91	36.90		39.38	39.43	
P		3.63			4.67			5.32	
Q		31.81			36.90			39.40	
R		64.56			58.43			55.28	
S		BzOH			BzOH			BzOH	

Table 1 (Continued)

A		78			79	
B		40°			40°	
C		NaBS			NaBS	
D	58.3421	58.2750	59.3623	58.3459	58.2745	59.3624
E	62.2021	63.3742	62.7592	62.9862	62.5628	63.9848
F	3.8600	5.0992	3.3969	4.6403	4.2883	4.6224
G	5.02	6.65	4.47	7.41	6.84	7.37
H	.1328	.1328	.1328	.1328	.1328	.1328
I	2.11	2.12	2.13	2.59	2.59	2.59
J	32.1897	30.2851		30.5457	30.5319	
K	37.4711	35.4257		36.5705	35.8822	
L	5.2814	5.1406		6.0248	5.3503	
M	34.1227	32.1666		32.9504	32.6684	
N	1.9330	1.8815		2.4047	2.1365	
O	36.61	36.61		39.92	39.93	
P		2.12			2.59	
Q		36.61			39.92	
R		61.27			57.49	
S		BzOH			BzOH	

Table 2 - Analysis of Wet Residues

A	Solids in Equilibrium with Run Number		23		26
B	Weight of Weighing Bottle	31.5583	33.9369	32.7783	31.6619
C	Weight Plus Sample	36.8605	38.1076	35.5904	33.3110
D	Weight of Sample	5.3022	4.1707	2.8121	1.6491
E	Ml. of NaOH Solution	26.05	20.42	38.91	22.75
F	Normality of NaOH Solution	.0963	.0963	.0813	.0813
G	% BzOH	5.43	5.41	13.74	13.70
H	Weight of Weighing Bottle		30.5332	31.5838	31.5577
I	Weight Plus Sample		38.8187	38.5413	36.2402
J	Weight of Sample		8.2855	6.9575	4.6825
K	Weight Plus Dried Sample		34.5972	34.9816	33.8455
L	Weight of Dried Sample		4.0640	3.3978	2.2878
M	% Salt		49.05	48.85	48.87
N	Average % BzOH		5.42		13.72
O	Average % Salt		49.05		48.86
P	% H_2O		45.53		37.42

Table 2 (Continued)

		48		49		50
A						
B		30.6795	58.3407	58.0404	58.3413	58.0410
C		36.6241	61.7603	62.6570	63.1031	62.6365
D		5.9446	3.4196	4.6166	4.7618	4.5955
E		62.26	34.43	46.52	34.69	33.53
F		.1114	.0980	.0980	.1109	.1109
G		14.22	12.05	12.09	9.87	9.88
H	32.0205	31.6626	31.8495	31.1011	31.6626	30.6790
I	39.8243	38.8853	40.6495	37.9129	38.7263	37.7969
J	7.8038	7.2227	8.8000	6.8118	7.0637	7.1179
K	36.0631	35.4028	36.5018	34.7056	35.4973	34.5498
L	4.0426	3.7402	4.6523	3.6045	3.8347	3.8708
M	51.81	51.79	52.87	52.92	54.30	54.37
N		14.22		12.07		9.88
O		51.80		52.90		54.33
P		33.98		35.03		35.89

Table 3 - Summary of Solubility Data*

1. System: H_2O, NaXS, BzOH @ 30°C.

Run No.	Wt. % BzOH	Wt. % NaXS	Wt. % H_2O	M·BzOH	M·NaXS	M'BzOH	M'NaXS	S, BzOH	Wt. %NaXS in NaXS soln.	Molality NaXS soln.	Gms. BxOH / Gm. NaXS corr.	Wt. %BzOH / .41
-	0.41	0.00	99.59	.034	.000	.034	.000	4.12	0.0	.000	$\frac{0}{0}$	1.00
1	1.10	14.56	84.34	.090	.699	.107	.829	11.12	14.7	.707	.052	2.68
2	1.65	19.34	79.01	.135	.929	.170	1.176	16.78	19.7	.944	.068	4.02
4	3.09	27.20	69.71	.253	1.307	.363	1.874	31.89	28.2	1.348	.103	7.54
5	4.34	32.89	62.77	.355	1.580	.566	2.517	45.37	34.4	1.651	.124	10.58
7	5.12	35.06	59.82	.419	1.684	.701	2.815	53.96	37.0	1.775	.139	12.49
12	0.00	28.75	71.25	.000	1.381	.000	1.938					
8	1.07	29.95	68.98	.088	1.439	.127	2.086					
9	2.36	31.62	66.02	.193	1.519	.293	2.301					
10	2.99	32.44	64.57	.245	1.558	.379	2.412					
11	3.66	33.26	63.08	.300	1.599	.476	2.537					

* Only points used in plotting graphs are tabulated. Many points are not plotted because they lie so close to those which are plotted.

Table 3 (Continued)

2 . **System:** H_2O, NaXS, BzOH @ 40°C.

Run No.	Wt. % BzOH	Wt. % NaXS	Wt. % H_2O	M,BzOH	M,NaXS	M'BzOH	M'NaXS	S,BzOH	Wt.%NaXS in NaXS soln.	Molality NaXS soln.	$\frac{\text{Gms. BzOH}}{\text{Gm. NaXS}}$ corr.	$\frac{\text{Wt.\%BzOH}}{0.55}$
-	0.55	0.00	99.45	.045	.000	.045	.000	5.53	0.0	.000	$\frac{0}{0}$	1.00
13	1.38	13.52	85.20	.113	.649	.133	.762	13.99	13.7	.658	.067	2.51
14	2.41	20.02	77.57	.197	.961	.254	1.239	24.70	20.5	.985	.099	4.38
15	3.30	24.06	72.64	.270	1.155	.372	1.591	34.13	24.9	1.196	.121	6.00
16	4.73	29.36	65.91	.387	1.410	.588	2.140	49.65	30.8	1.480	.149	8.60
17	5.59	32.48	61.93	.458	1.560	.739	2.519	59.21	34.4	1.652	.162	10.16
18	6.97	36.54	56.49	.571	1.755	1.010	3.107	74.92	39.3	1.886	.183	12.67
25	9.32	43.31	47.37	.763	2.080	1.612	4.391	102.77	47.8	2.294	.209	16.94
26	9.54	43.80	46.66	.781	2.104	1.674	4.508	105.46	48.4	2.326	.212	17.35
20	0.00	40.09	59.91	.000	1.930	.000	3.214					
21	2.69	41.85	55.46	.220	2.010	.397	3.624					
22	5.60	42.90	51.50	.459	2.060	.891	4.001					
24	8.35	43.37	48.28	.684	2.083	1.417	4.315					

Table 3 (Continued)

3. System: H_2O, NaXS, BzOH @ 60°

Run No.	Wt. % BzOH	Wt. % NaXS	Wt. % H_2O	M.BzOH	M.NaXS	M^1 BzOH	M^1NaXS	S,BzOH	Wt.%NaXS in NaXS soln.	Molality NaXS soln.	$\frac{\text{Gms.BzOH}}{\text{Gm. NaXS}}$ corr.	$\frac{\text{Wt.\%BzOH}}{1.18}$
33	1.18	0.00	98.82	.097	.000	.098	.000	11.94	0.0	.000	$\frac{0}{0}$	1.00
35	2.81	12.43	84.76	.230	.596	.271	.703	28.91	12.8	.614	.144	2.38
32	4.83	18.74	76.43	.396	.900	.517	1.177	50.76	19.7	.946	.209	4.09
31	8.98	27.17	63.85	.736	1.305	1.152	2.044	98.66	29.8	1.434	.303	7.61
30	10.34	30.15	59.51	.847	1.448	1.423	2.434	115.32	33.6	1.615	.320	8.76
34	13.28	35.15	51.57	1.087	1.688	2.109	3.274	153.14	40.5	1.946	.360	10.12
41	19.20	44.60	36.20	1.573	2.142	4.344	5.917	237.62	55.2	2.651	.421	16.27
40	20.39	46.00	33.61	1.670	2.210	4.969	6.574	256.12	57.8	2.775	.434	17.27
29	0.00	46.53	53.47	.000	2.235	.000	4.180					
37	5.07	47.40	47.53	.415	2.276	.874	4.790					
47	9.25	47.31	43.44	.758	2.272	1.744	5.231					
50 x	11.17	47.55	41.28									
36	11.68	47.36	40.96	.956	2.274	2.336	5.554					
49 y	13.38	47.20	39.42	1.096	2.267	2.781	5.750					
48 z	15.64	46.88	37.48	1.281	2.251	3.417	6.006					
x	9.88	54.33	35.89	Solids in Equilibrium								
y	12.07	52.90	35.03	" " "								
z	14.22	51.80	33.98	" " "								

Table 3 (Continued)

4. System: H_2O, NaBS, BzOH @ 40°

Run No.	Wt. % BzOH	Wt. % NaBS	Wt. % H_2O	M'BzOH	M'NaBS	S, BzOH	Molality NaBS soln.	$\frac{\text{Gms.BzOH}}{\text{Gm.NaBS}}$ corr.
64	0.92	21.06	78.02	.097	1.498	9.29	1.180	.023
62	1.62	32.11	66.27	.200	2.689	16.47	1.811	.039
78	2.12	36.61	61.27	.283	3.314	21.65	2.076	.049
79	2.59	39.92	57.49	.369	3.854	26.59	2.275	.057
59	3.11	42.40	54.69	.466	4.283	32.10	2.419	.067

5. System: H_2O, NaTS, BzOH @ 40°

Run No.	Wt. % BzOH	Wt. % NaTS	Wt. % H_2O	M'BzOH	M'NaTS	S, BzOH	Molality NaTS soln.	$\frac{\text{Gms.BzOH}}{\text{Gm.NaTS}}$ corr.
71	1.47	20.32	78.21	.154	1.338	14.92	1.062	.051
73	2.23	25.78	71.99	.254	1.845	22.81	1.358	.071
75	3.63	31.81	64.56	.460	2.537	37.66	1.700	.103
76	4.67	36.90	58.43	.655	3.252	48.99	1.993	.118
77	5.32	39.40	55.28	.788	3.671	56.20	2.144	.127

6. System: H_2O, Nam - XS, BzOH @ 40°

Run No.	Wt. % BzOH	Wt.%NamXS$_s$	Wt. % H_2O	M'BzOH	M'NamXS	S, BzOH	Molality NamXS soln.	$\frac{\text{Gms.BzOH}}{\text{Gm.NamXS}}$ corr.
70	1.75	19.18	79.07	.181	1.165	17.81	.938	.068
72	3.13	26.63	70.24	.365	1.821	32.31	1.320	.103
74	4.20	31.49	64.31	.535	2.352	43.83	1.578	.122
51	6.16	39.06	54.78	.921	3.425	65.64	2.000	.150

Table 3 (Continued)

7\. System: H_2O, NaCS, BzOH @ 40°

Run No.	Wt. % BzOH	Wt. % NaCS	Wt. % H_2O
69	1.05	8.22	90.73
68	2.14	14.77	83.09
67	4.20	25.27	70.53
63	4.91	28.74	66.35
65	7.54	40.64	51.82
66	11.54	53.10	35.36

8\. System: H_2O, NaBrBS, BzOH @ 40°

Run No.	Wt. % BzOH	Wt. % NaBrBS	Wt. % H_2O
57	1.18	15.52	83.40
60	2.68	24.95	72.37
58	4.28	32.50	63.22
61	4.79	34.99	60.22