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# Ternary Phase Diagram Determinations Concerning Potassium Electrolyte Influence On Aqueous Solutions Of Dioxane Or Tetrahydrofuran

John Albert McNaney  
*University of the Pacific*

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TERNARY PHASE DIAGRAM DETERMINATIONS CONCERNING  
POTASSIUM ELECTROLYTE INFLUENCE ON AQUEOUS  
SOLUTIONS OF DIOXANE OR TETRAHYDROFURAN

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A Dissertation

Presented to  
the Faculty of the Graduate School  
University of the Pacific

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In Partial Fulfillment  
of the Requirements for the Degree  
Doctor of Philosophy

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by  
John Albert McNaney

August 1967

This dissertation, written and submitted by

John Albert McNamey,

is approved for recommendation to the  
Graduate Council, University of the Pacific.

Department Chairman or Dean:

\_\_\_\_\_

Dissertation Committee:

Howard K. Zimmerman

Richard P. Dodge

Charles W. Foscoe

Paul G. G. G.

Wesley L. L.

Dated Aug 26, 1967

## ABSTRACT OF DISSERTATION

For the graphical representation of the mutual, partial solubilities of a ternary system, a diagram is generally employed which is based upon the equilateral triangle, whose properties are especially felicitous for this purpose.

In this study, the phase diagrams for the following systems were determined: potassium acetate-water-dioxane, potassium acetate-water-tetrahydrofuran, potassium benzoate-water-dioxane, potassium benzoate-water-tetrahydrofuran, potassium chloride-water-tetrahydrofuran, and potassium hydroxide-water-dioxane.

The systems, potassium acetate-water-dioxane and potassium hydroxide-water-dioxane, were investigated at 25° and 85°. This study indicates that they are, to a slight degree, temperature dependent. When these systems were plotted on a mole-percentage basis, it was found that both potassium compounds have about the same phase separating ability per molecule.

The solubility curves of potassium benzoate in water-dioxane and in water-tetrahydrofuran solutions were determined through the employment of a modified Schreinemakers "wet residue" method. It was established that this salt cannot stratify aqueous solutions of either dioxane or tetrahydrofuran into two liquid phases.

The phase diagram of potassium chloride-water-tetrahydrofuran was the only diagram, of those determined in this study, in which an invariant point was discovered. The reason such an invariant point exists is related to the fact that potassium chloride does not produce a salting-out effect through the full percentage composition range of this ternary mixture.

Other investigators have found that the greater the water solubility of a given alkali metal salt, the greater is its salting-out effect. The water solubility of the salts investigated in this study are compared as follows: potassium acetate >> potassium chloride > potassium benzoate. Potassium acetate was found to have the greatest capacity to stratify aqueous solutions of tetrahydrofuran and aqueous solutions of dioxane, potassium chloride has a lesser capacity to bring this about, and potassium benzoate cannot stratify these solutions.

Within the limits of precision available in this work, none of the electrolytes investigated was found to be soluble in either of the organic solvents employed.

## ACKNOWLEDGMENTS

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## CHAPTER I

### INTRODUCTION

The Phase Rule is a thermodynamic law, first stated by J. Willard Gibbs (8), relating the number of phases, the number of components, and the number of degrees of freedom, or the variance, of a system in heterogeneous equilibrium, in which it is assumed that the only determinative variables are temperature, pressure, and composition. It deals with the heterogeneous equilibria involved in processes which may be classified either as physical or as chemical, so long as they are dynamic and reversible in nature, in contrast with the nature of the static equilibria of mechanics. The various terms involved in the Phase Rule, although familiar, require explanation and limitation for their correct application.

A phase is one of the homogeneous, mechanically separable portions of a heterogeneous system. A system consisting of a liquid and a vapor is a two-phase system, as is also the mixture of a precipitate and its saturated solution; a system consisting of a solution and two saturating solids, with vapor, is in four phases. The number of components of a system is the number of independent variable constituents necessary for the statement of the composition of all its phases, such as the number of metals, for example, in an alloy. The number of degrees

of freedom ( $F$ ) is the number of internal or intensive variables, e.g., various concentrations, that is, in addition to temperature and pressure - which have to be specified in order to determine the state of the system completely. The Phase Rule states that if a heterogeneous system consisting of ( $C$ ) components in ( $P$ ) phases is in equilibrium, then  $F = C - P + 2$ . If a phase contains ( $C$ ) components, its composition involves  $C - 1$  independent percentage terms, so that the total number of internal variables, including temperature and pressure, is  $P(C - 1) + 2$ . But if the system is in heterogeneous equilibrium, the chemical potential of each component is the same in all phases containing it, so that there are accordingly  $C(P - 1)$  restricting conditions or equations inherent in the condition of equilibrium. Hence, the number of unrestricted variables, or the number of degrees of freedom,  $F$ , is  $P(C - 1) + 2 - C(P - 1)$ , or  $F = C - P + 2$  (23).

In three-component systems a single phase possesses four degrees of freedom, namely, temperature, pressure, and the composition of two out of three components. This number of variables poses great difficulty in the graphical presentation of the phase relations. For this reason, data in ternary systems are generally presented at some fixed pressure, such as atmospheric, and at constant temperatures. Under these conditions it is possible to show the concentration relations among the three compo-

nents at any given temperature on a planar diagram. By combining such planar diagrams for various temperatures it is then possible, if desired, to construct a three-dimensional model having concentrations as a base and temperature as a vertical axis.

For a three-component system the Phase Rule takes the form  $F = 5 - P$ . At a fixed pressure and temperature the number of degrees of freedom is reduced by two, so that  $F = 3 - P$ , and the maximum number of phases which can occur simultaneously is thus three. This is the same number as is possible in two-component systems under a constant pressure only. Therefore, under the specified conditions an area will indicate divariance, a line monovariance, and a point invariance (14).

For ternary systems in which the three components generally have the same relative importance, it is usual to employ an equilateral triangle to present graphically the phase relations (15). Such a triangle has the property that the sum of the lengths of the three perpendiculars from any interior point  $M$  to the three sides is constant and equal to the height  $h$  (Figure 1). If the height is taken as 1, and each of the perpendiculars  $Ma$ ,  $Mb$ ,  $Mc$ , is equal to the concentrations  $c_A$ ,  $c_B$ , and  $c_C$ , each point in the interior of the triangle will correspond to a definite composition in the ternary system. We are thus provided with a very satisfactory method of representing

the composition.

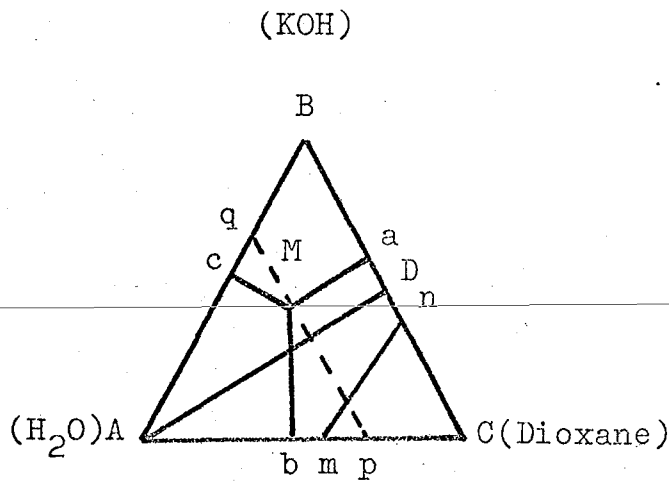


FIGURE 1

EXAMPLE OF THE TYPE OF GRAPH  
USED IN THIS STUDY

Obviously, the corners of the triangle correspond to the pure components, for at these points two of the perpendiculars to the sides of the triangle equal zero and the third is equal to unity. The percentage of a particular component, as C (Dioxane) in a mixture is obtained by finding the corresponding perpendicular distance from the point to the opposite side. The greater the distance of the point from C, the shorter  $M_c$  will be. When the length  $M_c$  becomes zero, the mixture contains no dioxane, and since the point lies on the side AB, it represents a mixture of B (KOH) with A ( $H_2O$ ). In a similar manner the side BC represents the mixtures of dioxane with KOH, and side AC, the mixture of dioxane with  $H_2O$ .

All mixtures whose compositions are represented by points on the line  $mn$ , which is parallel to  $AB$ , contain the same amount of dioxane, since the perpendicular distance from  $mn$  to  $AB$  is constant. Similarly, all mixtures which contain the same amount of  $KOH$  lie on a line parallel to  $AC$ , and all mixtures which lie on a line like  $AD$  that passes through the corner  $A$ , are characterized by a constant ratio of the other two components, dioxane and  $KOH$ , because for all points on such a line the ratio of the perpendicular distance to the sides  $AC$  and  $AB$  is the same.

The ratio of the perpendicular distance  $Ma$  (Figure 1) to the height  $AD$  is the same as the ratio  $qB$  ( $=pC$ ) to the length of the side  $AB$  ( $=AC$ ). For this reason it is immaterial in specifying the concentrations whether the height  $AD$  or one of the sides is taken as unity. In the one case, the concentration of  $A$  at the point  $M$  is read  $Ma$  and in the other,  $qB$  ( $=pC$ ).

In practice it is customary to express the concentrations in percent, that is, the sum of the three concentrations is set equal to 100. The sides of the triangle are divided into 100 parts to provide a scale for indicating the concentration of each constituent. In order to obtain the concentration in  $A$  of a point  $M$ , a line  $pq$  is drawn parallel to the opposite side  $BC$  and the distance  $pC$  (or  $qB$ ) of the intersections of this line with the sides from

the corners B and C is measured off. The ratio of pC to the length of a side then represents the concentration in A of a mixture corresponding in composition to the point M.

Although we are indebted to J. Willard Gibbs (8) for the first enunciation of the Phase Rule, it was not until 1887 that its practical applicability to the study of chemical equilibria was made apparent. In that year Roozeboom disclosed the great generalization, which for upwards of ten years had remained hidden and unknown save to a very few, by stripping from it the garb of abstract mathematics in which it had been clothed by its first discoverer. The Phase Rule was thus made generally accessible; and its adoption by Roozeboom as the basis of classification of the different cases of chemical equilibrium then known established its value, not only as a means of coordinating the large number of isolated cases of equilibrium and of giving a deeper insight into the relationships between the different systems, but also as a guide in the investigation of unknown systems (6).

The theory of multicomponent systems was further developed by N. S. Kurnakov, the founder of modern physicochemical analysis, whose easily visualized geometric method of describing and analyzing various binary and certain ternary systems has played an exceptionally important role in physicochemical research. Analytic and

geometric methods of treating systems of two and three components, and, in several cases, more than three components have also been developed by other scientists (Mendeleev, Konovalov, Schröder, Aleksyev, Le Chatelier, Roozeboom, Tammann, Stepanov, Schreinemakers, Masing, Radishchev, Ageyev, Pogodin, Bekker, Pines, Storonkin, Mlodzeyevskiy, Korzhinskiy, Danilov, Perel'man, Kamenetskaya, and others) (19).

Multicomponent systems are widespread in nature and in industry. Examples include rocks, minerals, and ores, sea water, and salt-lake brines. Many technical alloys and semi-conducting materials, heat transfer agents and electrolytes, enamels and glasses, complex mineral fertilizers, and catalysts are multicomponent systems. The study of systems containing these components is greatly facilitated when geometric methods are used to summarize the experimental data. Moreover, graphs are generally concise and readily understood, and permit quantitative calculations, interpolation, and extrapolation. It thus becomes possible to predict the properties of multicomponent composition on the basis of data on lower constituent systems from the same starting materials, and this is of considerable practical importance (20).

The phenomena which gave rise to this study were first brought to the attention of Dr. Howard K. Zimmerman, Director of Aminosugar Research at the University of the



Pacific, by research workers in peptide chemistry where the potassium hydroxide-dioxane-water system was used in the saponification of esters. It was then used in this laboratory to saponify sugar acetates and benzoates and proved to be a very mild reagent. Aminosugar derivatives, even hydrochlorides of aminosugar glycosides, can be ~~extracted with dioxane or tetrahydrofuran from concentrated~~ aqueous potassium chloride solutions. Thus a fast and convenient desalting process was made available for these compounds. In the past the desalting of water soluble aminosugar derivatives could only be achieved by costly and elaborate ion exchange chromatography.

In the mild saponification procedure mentioned above, such a salting-out of dioxane was observed on several occasions. Since this salting-out effect can be quite troublesome in carrying out the saponification, it became necessary to initiate a complete study of the three compound system in order to learn how such a salting-out effect might be avoided.

With regard to the salting-out effect of the tetrahydrofuran-water systems, it was also highly desirable to learn how better to control the salting-out effect in liquid-liquid immiscibility in order to perform solvent extractions in such a mixed pair of solvents. To help facilitate work in this area, a complete picture of the phase relationships in solvent systems utilized therein

was required.

An outline of this study includes:

1. Determination of the phase diagrams for the systems involving the following compounds:

$KC_2H_3O_2$ .....Potassium Acetate

$KC_7H_5O_2$ .....Potassium Benzoate

$KCl$ .....Potassium Chloride

$KOH$ .....Potassium Hydroxide

in each of the following two-solvent systems:

Dioxane-Water, Tetrahydrofuran-Water

2. Determination of the temperature dependence of these diagrams where feasible.
3. An attempt to provide a theoretical explanation for the experimental results obtained.

Potassium chloride was investigated only in the tetrahydrofuran-water system and experiments with potassium hydroxide were made only with the dioxane-water system.

Mr. Eugene Chulik has assisted in the foregoing work by developing analytical means for quantitative determination of acetate and benzoate salts, as modifications of the method of D. Ceausescu (4), in samples obtained from the above mentioned systems.

## CHAPTER II

### EXPERIMENTAL PROCEDURES AND RESULTS

The diverse nature of the systems studied made it necessary to use two different methods in this work. A general description of each method used is as follows. Various concentrations of potassium electrolyte-water solutions were put in a constant-temperature bath and then were titrated with a cyclic ether component until the system became turbid, which indicated the separation of the solution into two liquid phases, as detected visually or until a precipitate, which denoted a solid phase, made its appearance.

Two liquid phase separations were found in the following types of systems: potassium hydroxide-water-dioxane, potassium acetate-water-dioxane, potassium acetate-water-tetrahydrofuran, and potassium chloride-water-tetrahydrofuran. In the latter, however, a solid phase was observed at low tetrahydrofuran concentrations.

After ascertaining the liquid-liquid miscibility region within which two liquid phases were found, it was then possible arbitrarily to select a mixture of the three components falling within this region, allow them to mix in a constant-temperature bath until they reached equilibrium, transfer the mixture to a separatory funnel whose temperature was the same as the equilibrium temperature,

where they were separated and then each layer was analyzed. In this manner the liquid-liquid tie-lines could be established which confirmed the accuracy of the miscibility gap obtained by the method described in the preceding paragraph.

The systems potassium benzoate-water-dioxane and potassium benzoate-water-tetrahydrofuran did not separate into two liquid phases. In these two cases, and, in part of the previously mentioned potassium chloride-water-tetrahydrofuran system, a solid phase was observed. A solubility curve was determined for these systems also. In order to establish the composition of the solid precipitate, Schreinemakers "wet residue" method (25), with the modifications of that method which have been introduced by Hill and Ricci (11), was followed. In Schreinemakers method of "wet residues" a tie-line is determined by analyzing the saturated solution and also a sample of the solid phase still wet with the mother liquor. This wet residue must be a point fixing a line joining the composition of the liquid at the saturated solution point and the solid phase. The method suggested by Hill and Ricci differs from the classical Schreinemakers method in that, instead of analyzing the wet residue, a ternary mixture of known composition (a known, synthetic total complex) is made up corresponding to a point within the solid-liquid two-phase region. Then the tie-line can be fixed by anal-

ysis of the saturated solution at equilibrium. Graphical or algebraic extrapolation of a set of tie-lines to their point of intersection determined the composition of the solid, which is in equilibrium with any matched pair of saturated solutions that are in equilibrium with each other, without the necessity of its separation from the mother liquor for chemical analysis. The establishment in this manner of the compositions of the saturated solutions in equilibrium with each other provide a means of cross checking liquid-liquid tie-line determination in cases where they occur in such a system.

#### I. APPARATUS USED

The major pieces of apparatus used in this study were the following: an oil bath, consisting of a cylindrical tank with the dimensions, 18" diameter x 18" height, in an insulated box with an electronic relay, used in conjunction with a micro-set thermoregulator, both manufactured by Precision Scientific Company; a circulating type constant-temperature bath manufactured by Lab-Line, a class A-type automatic buret made by Kimax Glass Company, three class A 50 ml burets, with Teflon stopcocks, also manufactured by Kimax Glass Company; and a Pyrex water-jacket type reaction flask.

## II. CHEMICALS USED

Potassium Acetate: Potassium acetate from J. T. Baker Chemical Company, 'Baker Analyzed' Reagent, assay 99.0% pure, was dissolved in CO<sub>2</sub>-free distilled water. This concentrated solution was standardized by titration with standard perchloric acid in glacial acetic acid where methyl violet was used as an indicator (7).

Potassium Benzoate: Potassium benzoate was synthesized by reacting stoichiometric amounts of 'Baker Analyzed' Reagent, assay 85.9% potassium hydroxide and 'Baker Analyzed' Reagent, assay 99.9% benzoic acid. The product was evaporated to dryness and then dissolved in CO<sub>2</sub>-free distilled water. This concentrated solution, as in the case of potassium acetate, was standardized with standard perchloric acid in glacial acetic acid where methyl violet was used as an indicator.

Potassium Chloride: Potassium chloride from J. T. Baker Chemical Company, 'Baker Analyzed' Reagent, assay 99.9% pure, was used as received.

Potassium Hydroxide: Potassium hydroxide from J. T. Baker Chemical Company, 'Baker Analyzed' Reagent, assay 85.9% pure was dissolved in CO<sub>2</sub>-free distilled water. This solution was standardized with potassium acid

phthalate.

Dioxane: Technical 1, 4-dioxane from J. T. Baker Chemical Company was purified by distillation over metallic sodium as described by Vogel (28). The product was kept in tightly stoppered brown glass bottles.

Tetrahydrofuran: Tetrahydrofuran, obtained from J. T. Baker Chemical Company, 'Baker Analyzed' Reagent, density 0.881, boiling range 65.8-66.4°C, was used as received.

Karl Fischer Reagent: Karl Fischer Reagent, standardized so that one milliliter of the reagent would react with at least five milligrams of water, was obtained from Allied Chemical Company.

Fisher Certified Standard Water In Methanol: Standard water in methanol, one milliliter = one milligram of water, was used to standardize the Karl Fischer Reagent and was obtained from the Fisher Scientific Company. It was necessary to restandardize the water in methanol standard.

### III. DETAILED PROCEDURE

The detailed procedure for obtaining the data necessary in order to determine the phase diagrams investigated is described below.

The thermoregulator, required to keep the oil bath in an isothermal condition, was adjusted for the desired temperature for the titration. The bath was then allowed to come to that temperature. In the systems, potassium hydroxide-water-dioxane and potassium acetate-water-dioxane, the densities of all components were determined as well as the normality of each aqueous potassium compound solution. It was then possible to mix known volumes and, hence, a known weight of one potassium compound with a known weight of water. This solution was placed, together with a stirring bar, in a 100-ml beaker which, in turn, was stirred on top of a water-operated immersion-type stirrer in the oil bath (see Figure 2, page 46). A light, constructed within the bath housing and above the oil surface, was focused on the solution. Next, a 50-ml buret was filled with dioxane and clamped above the stirred solution so that this liquid could be slowly added to the contents of the beaker. The titration was then begun and was continued until the solution became turbid. At this point, the volume of the titrant added was noted.

Table I, page 41, provides a characteristic example of the data for the experimental observations in the system potassium acetate-water-dioxane.

The data obtained for these systems were used in plotting solubility curves at temperatures of 25°C and 85°C on three-component, equilateral triangular graphs



(Figures 4 and 9, pages 48 and 53, respectively).

Tie-lines were then established according to the following procedure. A mixture of the three components, whose total composition was a point within the two-phase region of the graph, was put in a beaker with a stirring bar and placed in the oil bath. This mixture was agitated for eight hours at 25°C in order to permit the system to attain equilibrium. The two-phase liquid mixture was then poured into a separatory funnel and separated. Two samples were taken from the less dense layer and weighed. One was analyzed for the potassium compound and the other for water. This was repeated for the more dense layer. In the system, potassium hydroxide-water-dioxane, potassium hydroxide was determined by titration with standard hydrochloric acid while in the system, potassium acetate-water-dioxane, a standard perchloric acid in glacial acetic acid titration was employed in the potassium acetate determination (7). In both systems, water content was obtained by titration with standard Karl Fischer Reagent (16). Having found the weight percentage of two of the three components, the dioxane was determined by difference in each case.

An example of the foregoing data obtained in the system initially composed of 10% potassium hydroxide, 50% water, 40% dioxane is given in Table VI, page 45.

Solubility curves for the systems potassium benzoate-

water-dioxane and potassium benzoate-water-tetrahydrofuran as reflected in Tables III and IV, page 43, and in Figures 6 and 7, pages 50 and 51, respectively, were plotted at 25°C in the same manner as in the two systems already described. In the latter cases, however, the addition of a cyclic ether to the potassium benzoate-water solution resulted in the appearance of a solid precipitate, rather than a second liquid phase.

In order to ascertain the composition of the solid precipitate, a mixture of the three components, whose total composition correspond to a point within the solid-liquid two-phase region of the preliminary graph, was put in a stoppered flask, together with a stirring bar, and placed in the oil bath. This mixture was agitated for eight hours at 25°C in order to permit the system to attain equilibrium. The solid was then separated from the saturated liquid by filtration at the temperature of the equilibrium mixture. Two samples were taken from the liquid phase. One was analyzed for potassium benzoate by titration with a standard solution of perchloric acid in glacial acetic acid (7) and the other was analyzed for water content by titration with standard Karl Fischer Reagent. Having found the weight percentage of two of the three components, the cyclic ether content was then determined by difference in each case. This procedure was repeated at various points within the solid-liquid two-

phase region.

Table III, page 43, presents in two columns for each of the components the initial composition and the composition of the saturated solution, respectively.

The high volatility of tetrahydrofuran made it necessary to utilize a different apparatus in determining the diagrams of the systems, potassium acetate-water-tetrahydrofuran and potassium chloride-water-tetrahydrofuran. Because stoppered flasks had to be used in titrating the tetrahydrofuran into the potassium compound-water solutions, it became impossible to note turbidity when the oil bath was used. Instead, a circulating constant-temperature water bath was utilized. This bath was connected with rubber tubing to a water jacket type reaction flask (see Figure 3, page 47) into which predetermined solutions of the potassium compound-water and a stirring bar were deposited. A buret, containing the tetrahydrofuran, was clamped above the flask and its tip was inserted through a cork stopper in the neck of the flask. This flask rested on electric, magnetic type stirrer.

In the case of potassium acetate-water-tetrahydrofuran, except for the use of the circulating water jacket, data were obtained at 25° in the same manner and tabulated in the same manner as described for the system, potassium acetate-water-dioxane. For most of the potassium chloride-water-tetrahydrofuran work this was also the method fol-

lowed, except that potassium chloride was analyzed by the Mohr method of titration (3). At low concentrations of tetrahydrofuran in this system, however, a solid precipitate of potassium chloride was observed. The procedure followed and the tabulation used, from this point and thereafter were the same as those used for the systems, ~~potassium benzoate-water-dioxane and potassium benzoate-water-tetrahydrofuran~~ (see Table V, page 44). Such a phase behavior has as a consequence an invariant point in the solubility curve. In order to confirm the existence of this invariant point, synthetic mixtures of the three components were arbitrarily chosen to correspond to two points within the solid-liquid-liquid three-phase area. these mixtures were allowed to come to equilibrium for eight hours at 25°C. The stirrer was then turned off. After the solid had settled out, two samples of the more dense liquid were weighed and analyzed, the one for potassium chloride by use of standard silver nitrate titration, and the other for water content by Karl Fischer Reagent titration. This procedure was then repeated for the less dense liquid layer. Having found the weight-percentage of two of the three components, the tetrahydrofuran concentration was determined by difference.

## IV. TREATMENT OF DATA

From the recorded data it was possible to determine the solubility curves for each system, the liquid-liquid tie-lines, the solid-liquid tie-lines, and to confirm the invariant point found in one of the solubility curves.

Solubility Curves. The solubility weight-percentages are tabulated in Tables I-VI, pages 41-45. Each experimental point on any of the solubility curves was obtained from the predetermined individual weights of the potassium compound and water plus the weight of the cyclic ether titrated into this solution.

All such points formed smooth curves when plotted on the three-component triangular graphs used for each system investigated, except that of the potassium chloride-water-tetrahydrofuran system. In the latter case, two solubility curves appeared which met in an invariant point. The solubility plots are shown in Figures 4-9, pages 48-53.

Liquid-Liquid Tie-Lines. The weight-percentages of the mixtures, arbitrarily chosen as points within the two-phase liquid-liquid regions and found in four of the systems studied, are tabulated in Tables I, II, V, and VI; pages 41, 42, 44, and 45, respectively. Tabulated in the same tables are the weight-percentages of the three components found in each of the two liquid layers which resulted

from each of the chosen mixtures mentioned above.

Plots of the three points: original mixture, more dense layer, and less dense layer were made on the graph which already contained their solubility curve. Each set of these three points determined a straight line whose end points, corresponding to the more dense layer and less dense layer, respectively, fell on the solubility curve. These tie-line plots are shown in Figures 4, 5, 8, and 9; pages 48, 49, 52, and 53, respectively.

#### Representative Calculations:

##### Original Mixture Composition

Potassium Acetate 9.94%, Water 29.90%, Dioxane 60.16%

##### More Dense Phase Analysis

###### Water Determination

Titration of 0.0941g sample required 9.17ml of Karl Fischer Reagent (1 ml KFR = 5.66mg water).

$$9.17\text{ml} \times 0.00566\text{g/ml} = 0.0520\text{g}$$

$$0.0520\text{g}/0.0941\text{g} = 55.15\% \text{ water}$$

###### Potassium Acetate Determination

Titration of 0.6471g sample required 15.74ml of 0.0951 N  $\text{HClO}_4$ .

$$0.01574 \text{ liter} \times 0.0951 \text{ eq./liter} = 0.001495 \text{ eq.}$$

$$0.001495 \text{ eq.} \times 98.14\text{g/eq. (G.M.W.)} = 0.01469\text{g}$$

$$0.01469\text{g}/0.6471\text{g} = 22.70\% \text{ potassium acetate}$$

###### Dioxane Determination

$$100.00 - 55.15 - 22.70 = 22.15\% \text{ dioxane}$$

## Less Dense Phase Analysis

### Water Determination

Titration of 0.5154g sample required 8.5ml of Karl Fischer Reagent.

$$8.5\text{ml} \times 0.00566\text{g/ml} = 0.0482\text{g}$$

$$0.0482\text{g}/0.5154\text{g} = 9.35\% \text{ water}$$

### Potassium Acetate Determination

Titration of 8.1321g sample required 11.6ml of 0.0951 N  $\text{HClO}_4$ .

$$0.0116 \text{ liter} \times 0.0951 \text{ eq./liter} = 0.001101 \text{ eq.}$$

$$0.001101 \text{ eq.} \times 98.14\text{g/eq.} = 0.1081\text{g}$$

$$0.1081\text{g}/8.1321\text{g} = 1.33\% \text{ potassium acetate}$$

### Dioxane Determination

$$100.00 - 9.35 - 1.33 = 89.32\% \text{ dioxane (see Table I, page 41)}$$

Solid-Liquid Tie-Lines. Tabulated in Tables III, IV, and V; pages 43 and 44, are the weight-percentages of the originally prepared complexes which were chosen as points within the two-phase solid-liquid regions in three of the systems investigated. The weight-percentages of the saturated solutions, for each of the original complexes are also presented in these tables.

The data mentioned above were plotted on three-component triangular graphs. A slightly curved solubility line resulted from the plots of the saturated solution

points in each system. Straight lines were drawn connecting each prepared complex point with its corresponding saturated solution point. When extrapolated, all of these straight lines in each system met, approximately, in a point, the composition of the dissolved solid in the saturated solutions (25). These plots are shown in Figures 6, 7, and 8; pages 50, 51, and 52, respectively.

Representative Calculations:

Original Complex Composition

Potassium Benzoate 9.10%, Water 5.76%, Dioxane 85.10%

Saturated Solution Analysis

Water Determination

Titration of 1.0320g sample required 10.75ml of Karl Fischer Reagent (1 ml KFR = 5.93mg water).

$$10.75\text{ml} \times 0.00593\text{g/ml} = 0.0639\text{g}$$

$$0.0639\text{g}/1.0320\text{g} = 6.19\% \text{ water}$$

Potassium Benzoate Determination

Titration of 5.1600g sample required 3.74ml of 0.0964 N  $\text{HClO}_4$ .

$$0.00374 \text{ liter} \times 0.0964 \text{ eq./liter} = 0.00036 \text{ eq.}$$

$$0.00036 \text{ eq.} \times 160.20\text{g/eq. (G.M.W.)} = 0.0576\text{g}$$

$$0.0576\text{g}/5.1600\text{g} = 1.11\% \text{ potassium benzoate}$$

Dioxane Determination

$$100.00 - 6.19 - 1.11 = 92.70\%$$



## Algebraic Extrapolation Of The Tie-Lines

|                      | % Complex | % Saturated Solution |
|----------------------|-----------|----------------------|
| A Potassium Benzoate | 9.10      | 1.11                 |
| B Water              | 5.76      | 6.19                 |
| C Dioxane            | 85.10     | 92.70                |

92.70 parts of C contain 1.11 parts A + 6.19 parts B

85.10 parts of C contain 1.02 parts A + 5.70 parts B

$$\left. \begin{array}{l} 9.10 \text{ A} - 1.02 \text{ A} = 8.08 \text{ A} \\ 5.76 \text{ B} - 5.70 \text{ B} = 0.06 \text{ B} \end{array} \right\} 8.14 \text{ Total}$$

$$\text{A} = 99.3\%, \text{ B} = 0.7\% \text{ (see Table III, page 43)}$$

The modification of Schreinemakers "wet residue" Method which was used in this part of the investigation is outlined below.

Instead of analyzing the wet residue a complex is prepared of known composition and the solution only is analyzed. This, again gives two points on the diagram; the solution point on the curve and the complex point which replaces the wet residue point. Hill and Ricci (11) say that the complex method is as accurate or more accurate than the residue method if algebraic extrapolation of the tie lines is used.

Suppose the synthetic complex to be:

Compound A .....20%  
 Water B .....30%  
 Dioxane .....50%

and the solution on analysis gives:

A ..... 4%

B .....16%

Dioxane .....80%

80 parts dioxane contain  $4A + 16B$

50 parts dioxane contain  $2.5A + 10B$

This amount of solution is subtracted from the complex  
giving

$$\left. \begin{array}{l} 20 - 2.5 = 17.5 \text{ A} \\ 30 - 10.0 = 20.0 \text{ B} \end{array} \right\} 37.5 \text{ Total}$$

Thus, if all the dioxane could be removed from the complex  
as solution, the residue would be

46.7% A

53.3% B

This point, when marked on the edge of the diagram, gives  
the correct extrapolation of the complex point. It does  
not necessarily represent any existing solid phases, but  
the line joining this point to the solution point must  
pass through the true solid phase (22). In this investi-  
gation, however, all extrapolations ended with the solid  
phase as the pure potassium compound at one corner, i. e.,  
 $A = 100\%$ ,  $B = 0\%$ .

Invariant Point Confirmation. The weight-percentages  
of the prepared complexes, arbitrarily chosen within the  
three-phase solid-liquid-liquid region, are tabulated in

Table V, page 44. Tabulated in the same table are the weight-percentages of the more dense liquid layers and those of the less dense liquid layers.

Plots of each set of data: prepared complex, more dense layer, and less dense layer were made on the graph which already contained the solubility curve and tie-lines. A straight line was drawn from the prepared complex point to its more dense layer point and, similarly, from the complex point to the less dense layer point. This formed an angle with the complex point as the vertex. The ends of the two sides - more dense layer point and less dense layer point - fell on the solubility curve with the more dense point approximately on the invariant position. A plot of the other set of data gave similar results. This more dense layer point also coincided with the invariant point, confirming it, while the less dense layer point fell almost exactly on the previously plotted less dense layer point. These plots may be found in Figure 8, page 52.

## CHAPTER III

### DISCUSSION OF RESULTS

It has been well established that dioxane in an aqueous solution is associated with water (9, 10, 24, 27, 29). Evidence that tetrahydrofuran behaves in a like manner has also been reported (17).

According to Godneva and Klocho (9), when an electrolyte is added to water-dioxane or water-tetrahydrofuran mixtures, two phases result. In order to bring about this separation by the action of a salt or other electrolyte, the water-cyclic ether association must be broken down. The authors believe that the hydration of the electrolyte cations is accomplished by the dehydration of the cyclic ether molecules, causing this separation.

#### I. SALTING-OUT EFFECTS IN WATER-DIOXANE MIXTURES ATTRIBUTABLE TO POTASSIUM ACETATE OR POTASSIUM HYDROXIDE

The systems, potassium acetate-water-dioxane (Figure 4, page 48, Table I, page 41) and potassium hydroxide-water-dioxane (Figure 9, page 53, Table VI, page 45) were investigated at temperatures of 25° and 85°, respectively. The salting-out isotherms are binodal curves which were found to be slightly displaced toward the aqueous corner with an increase in temperature.

Then the temperature increases, it somewhat decreases the area of homogeneity (range of compositions comprising

a single phase) of the system studied. It appears that the higher temperature weakens the hydrogen bond between the water and non-aqueous solvent, relative to the hydrogen bonding at the lower temperature, and also lowers the degree of hydration of the cations but the latter takes place at a slower rate (9).

According to weight percentage diagrams, potassium hydroxide appears to have the greater ability in causing the separation of aqueous dioxane into two liquid phases. When this phase diagram is plotted in mole-percentages, however, the curves fall quite close to each other, indicating about the same degree of separating ability per molecule (see Figure 10, page 54).

Both potassium hydroxide and potassium acetate were found to be practically insoluble in dioxane. Their solubilities in water were ascertained. The results obtained approximate, within acceptable experimental error, the empirical literature values (see Table I and Table VI, pages 41 and 45, respectively).

## II. SALTING-OUT EFFECTS IN WATER-DIOXANE AND WATER-TETRAHYDROFURAN CONTAINING POTASSIUM ACETATE

The liquid layer formation (salting-out effect) isotherm (at 25°) of the system, potassium acetate-water-tetrahydrofuran is also a binodal curve (Figure 5, page 49). There is, however, a substantial difference between

the layering effect on the water-dioxane by potassium acetate compared to its effect on the water-tetrahydrofuran mixture. In the latter case, much less potassium acetate is required to bring about separation into two liquid phases than with the same percentage composition of water-dioxane. Even when plotted on a mole-percentage composition basis (see Figure 11, page 55) this difference, while less pronounced, still exists. One could conclude that the reason for this behavior rests in the fact that tetrahydrofuran has half the oxygen sites for hydrogen bonding that dioxane has and thus can hold less water in association. Previous experimenters, however, have produced results which seem to belie this. It has been postulated by different groups of investigators that the water-tetrahydrofuran association ratio is 17:1, water:tetrahydrofuran, (5, 21) as compared to 2:1, 3:1, and 4:1, water:dioxane, put forth by others (already cited; 24, 27). This study has determined that about three times as much potassium acetate, in mole-percentage, is required in order to cause stratification in dioxane than is necessary to obtain the same results in tetrahydrofuran when both solvents are in aqueous solutions. If tetrahydrofuran associates with more water than does dioxane, it would seem that the opposite should be true.

Some may feel that the difference in stratifying abilities is due to the stronger association of dioxane

molecules for each other than of the tetrahydrofuran molecules for each other.

On the other hand, it is also reasonable to conclude that, in comparison to dioxane, at 25<sup>o</sup>, tetrahydrofuran forms a weaker association with water and, hence, the cations can more easily break these bonds and cause liquid phase separation. The basis of this judgement rests with the assumption that 17 water molecules would be held less firmly by one tetrahydrofuran molecule than four water molecules by one dioxane molecule.

In an effort to establish a general relationship between the two solubility curves which might serve to unify one's understanding of them and reveal more about the properties of such systems, several graphical approaches were employed. The possibility of moving the potassium acetate-water-dioxane curve closer to the potassium acetate-water-tetrahydrofuran curve was first investigated. An attempt to build a model in terms equating the oxygen sites in dioxane to the oxygen site in tetrahydrofuran was made at first by plotting mole-percentage oxygen bridges. To accomplish this, the number of moles of oxygen bridges had to be considered as twice the number of moles of dioxane for a given point and the apparent molecular weight of the bridge taken as one half the dioxane molecular weight, 44.05.

After reworking the data and plotting the results,

the curves were found to lie even farther apart. This led to dividing the dioxane weight, in each case, by twice the molecular weight of the compound. Calculating "mole-percentages" on this basis, the curves were moved closer together. It was finally established that, if one divided the dioxane weight, in each case, by four times the molecular weight of dioxane, determined the number of moles of potassium acetate and of water in the usual manner, and plotted the pseudo-mole-percentages obtained, a curve resulted which fell almost exactly on the mole-percentage curve of potassium acetate-water-tetrahydrofuran.

Attempts were also made to bring the potassium acetate-water-tetrahydrofuran solubility curve closer to the potassium acetate-water-dioxane curve. In this endeavor, graphs were plotted, in mole-percentages, of potassium acetate-water and several hydrates of tetrahydrofuran;  $C_4H_8O \cdot H_2O$ ,  $C_4H_8O \cdot 2H_2O$ ,  $C_4H_8O \cdot 4H_2O$ , etc. All of these proved to be fruitless.

This investigation indicates that potassium acetate also is highly insoluble in tetrahydrofuran.

### III. POTASSIUM BENZOATE EFFECTS ON WATER-DIOXANE AND WATER-TETRAHYDROFURAN SOLUTIONS

Potassium benzoate does not bring about the formation of two liquid phases in aqueous solutions of either dioxane or tetrahydrofuran. The addition of dioxane or tetrahydro-



uran to a potassium benzoate-water solution, however, does result in a solid precipitate. This precipitate proved to be pure potassium benzoate. Although the solubility curves for both systems are almost identical (see Figures 6 and 7, pages 50 and 51), the precipitate of potassium benzoate was observed at slightly lower percentages in the system involving dioxane, that is, with the exception of the ends of this curve. When plotted in mole-percentages, however, the curves fall almost exactly on the same line.

This salt was also found to be insoluble in both dioxane and tetrahydrofuran. Its solubility in water was determined during this study and found to compare very favorably with established literature data (see Table III, page 43).

#### IV. SALTING-OUT EFFECT IN WATER-TETRAHYDROFURAN SOLUTIONS DUE TO POTASSIUM CHLORIDE

This system, in effect, is a combination of the two different types of systems already discussed (see Figure 5, page 49).

When tetrahydrofuran is added to a dilute potassium chloride-water solution, two liquid phases eventually appear. If the aqueous solution is increased in concentration of potassium chloride, one reaches a point when, at weight percentages of 22.6 potassium chloride, 71.0 water,

and 6.4 tetrahydrofuran, a solid precipitate appears which is in equilibrium with two liquid phases. At higher concentrations of potassium chloride, only a solid precipitate appears as the tetrahydrofuran is titrated into the solution. The precipitate was found to be pure potassium chloride.

An explanation of the above involves the linking together of all of the systems studied and previously discussed concerning potassium salts.

Kobzev (13) maintained, in a study of salts of potassium, sodium, lithium, rubidium, and cesium (all in aqueous solutions), that the solubility of a salt in water was related to its salting-out effect. He found that salts with the solubility from 6.4 to 2.8 gram equivalent weight per 100 ml of water at 25° caused stratification in all systems except water-methanol and water-ethanol. Salts with solubilities below 2.82 gram equivalent weights did not cause salting out.

The water solubility of the salts investigated in this study are, comparatively, as follows: potassium acetate  $\gg$  potassium chloride  $>$  potassium benzoate. As one might expect, then, potassium acetate has the greatest capacity to salt out aqueous solutions of dioxane and tetrahydrofuran. Potassium chloride is a borderline case and cannot bring about salting-out through the full percentage composition range of the ternary mixture.

Finally, potassium benzoate cannot cause two liquid phases to appear in either of these aqueous-cyclic ether solutions for it is insoluble in such solutions.

Potassium chloride, like the other potassium compounds studied, was found to be insoluble in tetrahydrofuran. The solubility of this salt in water was ascertained and compares very closely to the literature value (see Table V, page 44).

## CHAPTER IV

### SUMMARY

For ternary systems in which three components generally have the same relative importance, it is usual to employ an equilateral triangle to present graphically the phase relations.

In this study, the phase diagrams for the following systems were determined: potassium acetate-water-dioxane, potassium acetate-water-tetrahydrofuran, potassium benzoate-water-dioxane, potassium benzoate-water-tetrahydrofuran, potassium chloride-water-tetrahydrofuran, and potassium hydroxide-water-dioxane.

The systems, potassium acetate-water-dioxane and potassium hydroxide-water-dioxane, were investigated at 25° and 85°. This study indicates that they are, to a slight degree, temperature dependent. When these systems were plotted on a mole-percentage basis, it was found that both potassium compounds have about the same phase separating ability per molecule.

The solubility curves of potassium benzoate in water-dioxane and in water-tetrahydrofuran solutions were determined through the employment of a modified Schreinemakers "wet residue" method. It was established that this salt cannot stratify aqueous solutions of either dioxane or tetrahydrofuran into two liquid phases.

The phase diagram of potassium chloride-water-tetrahydrofuran was the only diagram, of those determined in this study, in which an invariant point was discovered. The reason such an invariant point exists is related to the fact that potassium chloride does not produce a salting-out effect through the full percentage composition range of this ternary mixture.

Other investigators have found that, the greater the water solubility of a given first row metal salt, the greater is its salting-out effect. The water solubility of the salts investigated in this study are as follows: potassium acetate  $\gg$  potassium chloride  $>$  potassium benzoate. Potassium acetate was found to have the greatest capacity to stratify aqueous solutions of dioxane and aqueous solutions of tetrahydrofuran, potassium chloride has a lesser capacity to bring this about, and potassium benzoate cannot stratify these solutions.

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## BIBLIOGRAPHY

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APPENDIX

TABLE I

SOLUBILITY CURVE AND TIE-LINE DATA FOR THE SYSTEM  
 POTASSIUM ACETATE-WATER-DIOXANE IN WT. %

| Solubility Curve Data                         |                  |         |   |                  |         |
|---|------------------|---------|---|------------------|---------|
| 25°C  |                  |         | 85°C  |                  |         |
| KC <sub>2</sub> H <sub>3</sub> O <sub>2</sub> | H <sub>2</sub> O | Dioxane | KC <sub>2</sub> H <sub>3</sub> O <sub>2</sub> | H <sub>2</sub> O | Dioxane |
| 0.33  | 14.15            | 85.52   | 0.36  | 15.74            | 83.90   |
| 0.53  | 16.15            | 83.32   | 0.59  | 17.99            | 81.42   |
| 5.14  | 34.96            | 59.90   | 5.69  | 38.53            | 55.78   |
| 8.68  | 43.32            | 48.00   | 9.43  | 47.16            | 43.41   |
| 15.50   | 51.70            | 32.80   | 15.95   | 54.50            | 29.55   |
| 24.35   | 53.10            | 22.55   | 24.59   | 53.64            | 21.77   |
| 29.93   | 55.44            | 14.63   |   |                  |         |
| 72.00   | 27.40            | 0.00    |   |                  |         |
| 71.00 <sup>20</sup>                           | (12)             |         |   |                  |         |
| 74.00 <sup>30</sup>                           | (Ibid.)          |         |   |                  |         |
| 72.93 <sup>25</sup>                           | (1)              |         |   |                  |         |

| Tie-Line Data 25°C                            |                  |         |   |                  |         |
|---|------------------|---------|---|------------------|---------|
| More Dense Layer                              |                  |         | Less Dense Layer                              |                  |         |
| KC <sub>2</sub> H <sub>3</sub> O <sub>2</sub> | H <sub>2</sub> O | Dioxane | KC <sub>2</sub> H <sub>3</sub> O <sub>2</sub> | H <sub>2</sub> O | Dioxane |
| 22.70   | 55.15            | 22.15   | 1.33  | 9.55             | 89.32   |
| 27.00   | 56.00            | 17.00   | 0.06  | 7.47             | 92.47   |
| 36.15   | 53.20            | 10.65   | 0.03  | 4.48             | 95.49   |
| 45.00   | 49.00            | 6.00    | 0.04  | 6.07             | 93.89   |
| 50.95   | 43.25            | 5.80    | 0.00  | 1.96             | 98.04   |
| 63.90   | 33.10            | 3.00    | 0.00  | 1.03             | 98.97   |
| 67.80   | 29.40            | 2.80    | 0.01  | 0.85             | 99.14   |

| Original Mixture                              |                  |         |
|---|------------------|---------|
| KC <sub>2</sub> H <sub>3</sub> O <sub>2</sub> | H <sub>2</sub> O | Dioxane |
| 9.94  | 29.90            | 60.20   |
| 14.80   | 34.95            | 50.20   |
| 25.00   | 39.90            | 35.10   |
| 39.80   | 45.00            | 15.20   |
| 39.90   | 35.60            | 24.50   |
| 34.10   | 18.75            | 47.15   |
| 38.50   | 17.60            | 43.90   |

TABLE II

SOLUBILITY CURVE AND TIE-LINE DATA FOR THE SYSTEM  
 POTASSIUM ACETATE-WATER-TETRAHYDROFURAN  
 IN WT. %

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 Solubility Curve Data 25°C
 

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| KC <sub>2</sub> H <sub>3</sub> O <sub>2</sub> | H <sub>2</sub> O | Tetrahyd. |
|---|------------------|-----------|
| 0.38  | 26.87            | 72.75     |
| 0.87  | 37.00            | 62.13     |
| 1.85  | 52.80            | 45.35     |
| 2.90  | 62.60            | 34.50     |
| 4.80  | 68.70            | 26.40     |
| 10.10   | 72.10            | 17.80     |
| 15.30   | 73.10            | 11.60     |
| 19.95   | 71.25            | 8.80      |
| 34.40   | 61.50            | 4.10      |
| 44.80   | 53.30            | 1.90      |

---

 Tie-Line Data 25°C
 

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| More Dense Layer                              |                  |           | Less Dense Layer                              |                  |           |
|---|------------------|-----------|---|------------------|-----------|
| KC <sub>2</sub> H <sub>3</sub> O <sub>2</sub> | H <sub>2</sub> O | Tetrahyd. | KC <sub>2</sub> H <sub>3</sub> O <sub>2</sub> | H <sub>2</sub> O | Tetrahyd. |
| 24.80   | 68.00            | 7.20      | 0.13  | 6.00             | 93.87     |
| 16.10   | 72.10            | 11.80     | 0.05  | 8.87             | 91.08     |
| 10.00   | 72.97            | 17.03     | 0.10  | 12.70            | 87.20     |
| 42.70   | 54.10            | 3.20      | 0.02  | 2.66             | 97.32     |
| 61.20   | 36.00            | 2.80      | 0.10  | 1.00             | 98.90     |

---

 Original Mixture
 

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| KC <sub>2</sub> H <sub>3</sub> O <sub>2</sub> | H <sub>2</sub> O | Tetrahyd. |
|---|------------------|-----------|
| 19.84   | 59.35            | 20.81     |
| 9.80  | 49.60            | 40.60     |
| 7.85  | 61.70            | 30.45     |
| 20.30   | 29.40            | 50.30     |
| 14.85   | 9.85             | 75.30     |

---

TABLE III

SOLUBILITY CURVE AND TIE-LINE DATA FOR THE SYSTEM  
 POTASSIUM BENZOATE-WATER-DIOXANE 25°C  
 IN WT. %

| Saturated Solution                            |                  |         | Original Complex                              |                  |         |
|---|------------------|---------|---|------------------|---------|
| KC <sub>7</sub> H <sub>5</sub> O <sub>2</sub> | H <sub>2</sub> O | Dioxane | KC <sub>7</sub> H <sub>5</sub> O <sub>2</sub> | H <sub>2</sub> O | Dioxane |
| 0.00  | 2.30             | 97.70   | 4.20  | 2.10             | 93.70   |
| 1.11  | 6.19             | 92.70   | 9.10  | 5.76             | 85.10   |
| 5.83  | 11.63            | 82.54   | 11.50   | 10.60            | 77.90   |
| 12.05   | 17.65            | 70.30   | 17.79   | 16.14            | 66.07   |
| 20.70   | 25.80            | 53.50   | 32.30   | 22.10            | 45.60   |
| 30.70   | 38.00            | 31.30   | 39.90   | 33.00            | 27.10   |
| 35.70   | 45.80            | 18.50   | 44.80   | 39.20            | 16.00   |
| 38.20   | 49.30            | 12.50   | 39.20   | 48.50            | 12.30   |
| 38.70   | 50.60            | 10.70   | 53.20   | 38.74            | 8.06    |
| 39.50   | 53.00            | 7.00    | 51.90   | 41.70            | 6.40    |
| 40.43   | 54.35            | 5.22    | 42.30   | 52.60            | 5.07    |
| 40.90   | 56.00            | 3.10    | 50.15   | 47.10            | 2.75    |
| 42.50   | 57.50            | 0.00    |   |                  |         |
| 42.40   | (18)             |         |   |                  |         |

TABLE IV

SOLUBILITY CURVE AND TIE-LINE DATA FOR THE SYSTEM  
 POTASSIUM BENZOATE-WATER-TETRAHYDROFURAN 25°C  
 IN WT. %

| Saturated Solution                            |                  |           | Original Complex                              |                  |           |
|---|------------------|-----------|---|------------------|-----------|
| KC <sub>7</sub> H <sub>5</sub> O <sub>2</sub> | H <sub>2</sub> O | Tetrahyd. | KC <sub>7</sub> H <sub>5</sub> O <sub>2</sub> | H <sub>2</sub> O | Tetrahyd. |
| 0.05  | 2.45             | 97.50     | 11.85   | 2.25             | 85.90     |
| 3.93  | 6.94             | 89.13     | 20.40   | 5.80             | 73.80     |
| 10.23   | 13.00            | 76.77     | 21.00   | 10.85            | 68.15     |
| 18.80   | 19.70            | 61.50     | 23.55   | 18.35            | 58.10     |
| 26.70   | 26.35            | 46.95     | 29.10   | 25.30            | 45.60     |
| 36.50   | 37.70            | 25.80     | 41.30   | 34.40            | 24.30     |
| 40.60   | 44.25            | 15.15     | 47.65   | 38.80            | 13.55     |
| 41.45   | 48.10            | 10.40     | 52.25   | 39.24            | 8.51      |
| 42.30   | 52.00            | 5.70      | 49.70   | 45.40            | 4.90      |
| 42.50   | 57.00            | 0.00      |   |                  |           |

TABLE V

SOLUBILITY CURVE AND TIE-LINE DATA FOR THE SYSTEM  
 POTASSIUM CHLORIDE-WATER-TETRAHYDROFURAN 25°C  
 IN WT. %

| Solubility Curve Data     |                  |           |                          |                  |           |
|---------------------------|------------------|-----------|--------------------------|------------------|-----------|
| Liquid-Liquid Equilibrium |                  |           | Solid-Liquid Equilibrium |                  |           |
| KCl                       | H <sub>2</sub> O | Tetrahyd. | KCl                      | H <sub>2</sub> O | Tetrahyd. |
| 0.63                      | 29.85            | 69.52     | 21.45                    | 71.50            | 7.05      |
| 1.39                      | 42.00            | 56.61     | 23.00                    | 70.70            | 6.30      |
| 3.65                      | 62.35            | 33.90     | 24.15                    | 72.10            | 3.75      |
| 7.28                      | 72.80            | 19.95     | 25.60                    | 73.00            | 1.40      |
| 11.05                     | 73.80            | 15.15     | 26.80                    | 72.90            | 0.00      |
| 14.85                     | 74.35            | 10.80     | 26.34                    | (26)             |           |
| 18.17                     | 72.83            | 8.98      |                          |                  |           |

| Tie-Line Data Liquid-Liquid Equilibrium |                  |           |                  |                  |           |
|---|------------------|-----------|------------------|------------------|-----------|
| More Dense Layer                        |                  |           | Less Dense Layer |                  |           |
| KCl                                     | H <sub>2</sub> O | Tetrahyd. | KCl              | H <sub>2</sub> O | Tetrahyd. |
| 7.90                                    | 68.40            | 23.70     | 0.01             | 13.80            | 86.19     |
| 13.20                                   | 73.60            | 13.20     | 0.00             | 9.95             | 90.05     |
| 16.20                                   | 73.30            | 10.50     | 0.00             | 8.72             | 91.28     |

| Original Mixture |                  |           |
|------------------|------------------|-----------|
| KCl              | H <sub>2</sub> O | Tetrahyd. |
| 5.00             | 50.00            | 45.00     |
| 10.05            | 59.95            | 30.00     |
| 9.97             | 50.05            | 39.98     |

| Solid-Liquid Equilibrium |                  |           |                  |                  |           |
|--------------------------|------------------|-----------|------------------|------------------|-----------|
| Saturated Solution       |                  |           | Original Complex |                  |           |
| KCl                      | H <sub>2</sub> O | Tetrahyd. | KCl              | H <sub>2</sub> O | Tetrahyd. |
| 23.20                    | 71.10            | 5.70      | 34.99            | 60.04            | 4.97      |
| 24.10                    | 71.50            | 4.40      | 31.10            | 65.00            | 3.90      |
| 24.95                    | 71.70            | 3.35      | 37.00            | 59.98            | 3.02      |

| Solid-Liquid-Liquid Equilibrium |                  |           |                  |                  |           |
|---------------------------------|------------------|-----------|------------------|------------------|-----------|
| More Dense Layer                |                  |           | Less Dense Layer |                  |           |
| KCl                             | H <sub>2</sub> O | Tetrahyd. | KCl              | H <sub>2</sub> O | Tetrahyd. |
| 22.60                           | 71.00            | 6.40      | 0.00             | 6.00             | 94.00     |
| 22.70                           | 70.95            | 6.37      | 0.00             | 6.10             | 93.90     |

| Original Complex |                  |           |
|------------------|------------------|-----------|
| KCl              | H <sub>2</sub> O | Tetrahyd. |
| 35.05            | 49.93            | 15.02     |
| 25.00            | 50.03            | 24.97     |

TABLE VI

SOLUBILITY CURVE AND TIE-LINE DATA FOR THE SYSTEM  
 POTASSIUM HYDROXIDE-WATER-DIOXANE IN WT. %

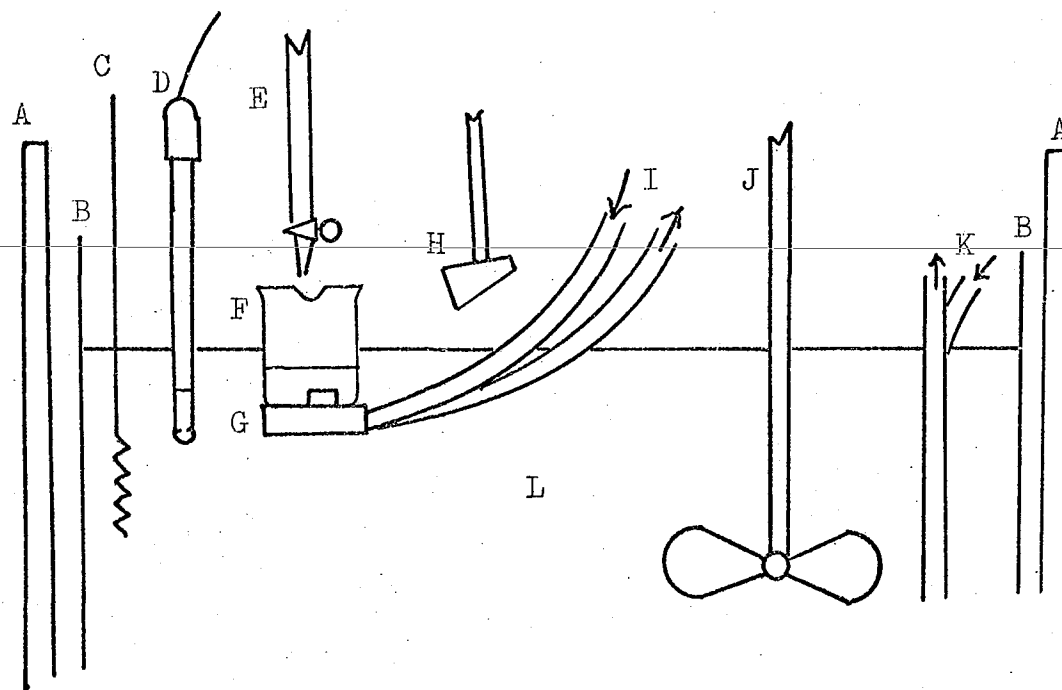
| Solubility Curve Data |                  |         |       |                  |         |
|-----------------------|------------------|---------|-------|------------------|---------|
| 25°C                  |                  |         | 85°C  |                  |         |
| KOH                   | H <sub>2</sub> O | Dioxane | KOH   | H <sub>2</sub> O | Dioxane |
| 0.31                  | 29.35            | 70.34   | 0.37  | 35.90            | 63.73   |
| 3.94                  | 49.45            | 46.61   | 1.40  | 39.10            | 59.50   |
| 11.65                 | 69.75            | 18.60   | 4.50  | 56.80            | 38.70   |
| 16.10                 | 72.60            | 11.30   | 11.90 | 71.80            | 16.30   |
| 25.60                 | 71.05            | 3.35    | 15.80 | 72.00            | 12.20   |
| 54.34                 | 45.66            | 0.00    |       |                  |         |
| 54.28                 | (2)              |         |       |                  |         |

| Tie-Line Data 25°C |                  |         |                  |                  |         |
|--------------------|------------------|---------|------------------|------------------|---------|
| More Dense Layer   |                  |         | Less Dense Layer |                  |         |
| KOH                | H <sub>2</sub> O | Dioxane | KOH              | H <sub>2</sub> O | Dioxane |
| 9.37               | 67.10            | 23.53   | 0.34             | 1.00             | 98.66   |
| 16.70              | 73.00            | 10.30   | 0.05             | 0.50             | 99.45   |
| 28.45              | 68.50            | 3.05    | 0.00             | 0.00             | 100.00  |
| 56.80              | 43.20            | 0.00    | 0.03             | 0.40             | 99.57   |

| Original Mixture |                  |         |
|------------------|------------------|---------|
| KOH              | H <sub>2</sub> O | Dioxane |
| 5.00             | 45.02            | 49.98   |
| 10.00            | 50.00            | 40.00   |
| 14.95            | 40.01            | 45.04   |
| 40.00            | 34.91            | 25.09   |



A. Box holding cylindrical tank containing oil bath. B. Cylindrical tank. C. Heating filament connected to relay. D. Thermoregulator connected to relay. E. Buret filled with cyclic ether. F. Beaker containing solution of potassium compound and water together with stirring bar. G. Water wheel type magnetic stirrer. H. Lamp focused on solution. I. Water inlet and outlet for magnetic stirrer. J. Oil bath circulator. K. Inlet and outlet used to send water through immersed copper coil when cooling of bath required. L. Oil.

FIGURE 2

SCHEMATIC ILLUSTRATION OF THE OIL BATH AND THE APPARATUS SETUP USED IN PART OF THIS STUDY.

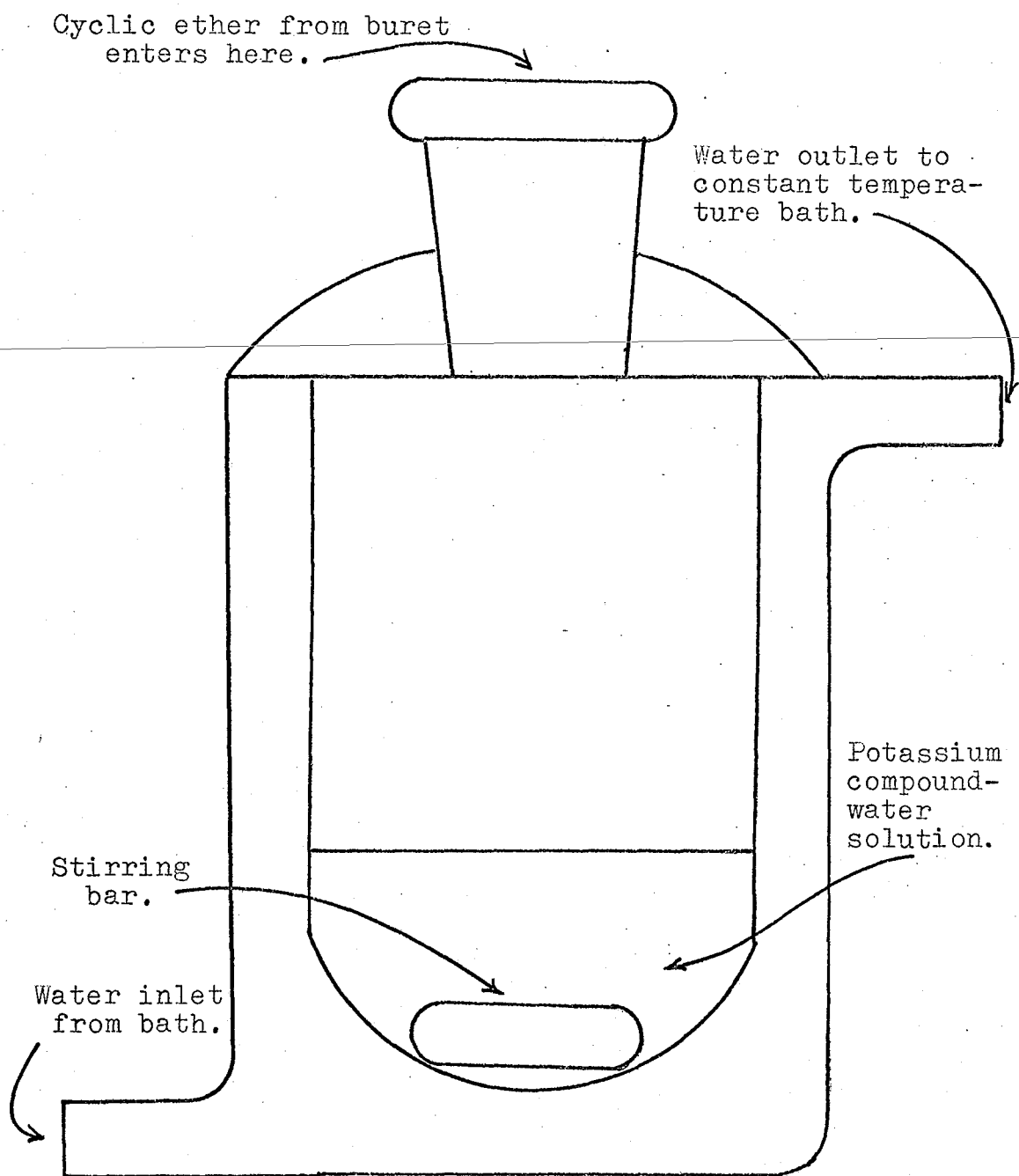


FIGURE 3

WATER JACKET TYPE REACTION FLASK  
AND CONTENTS



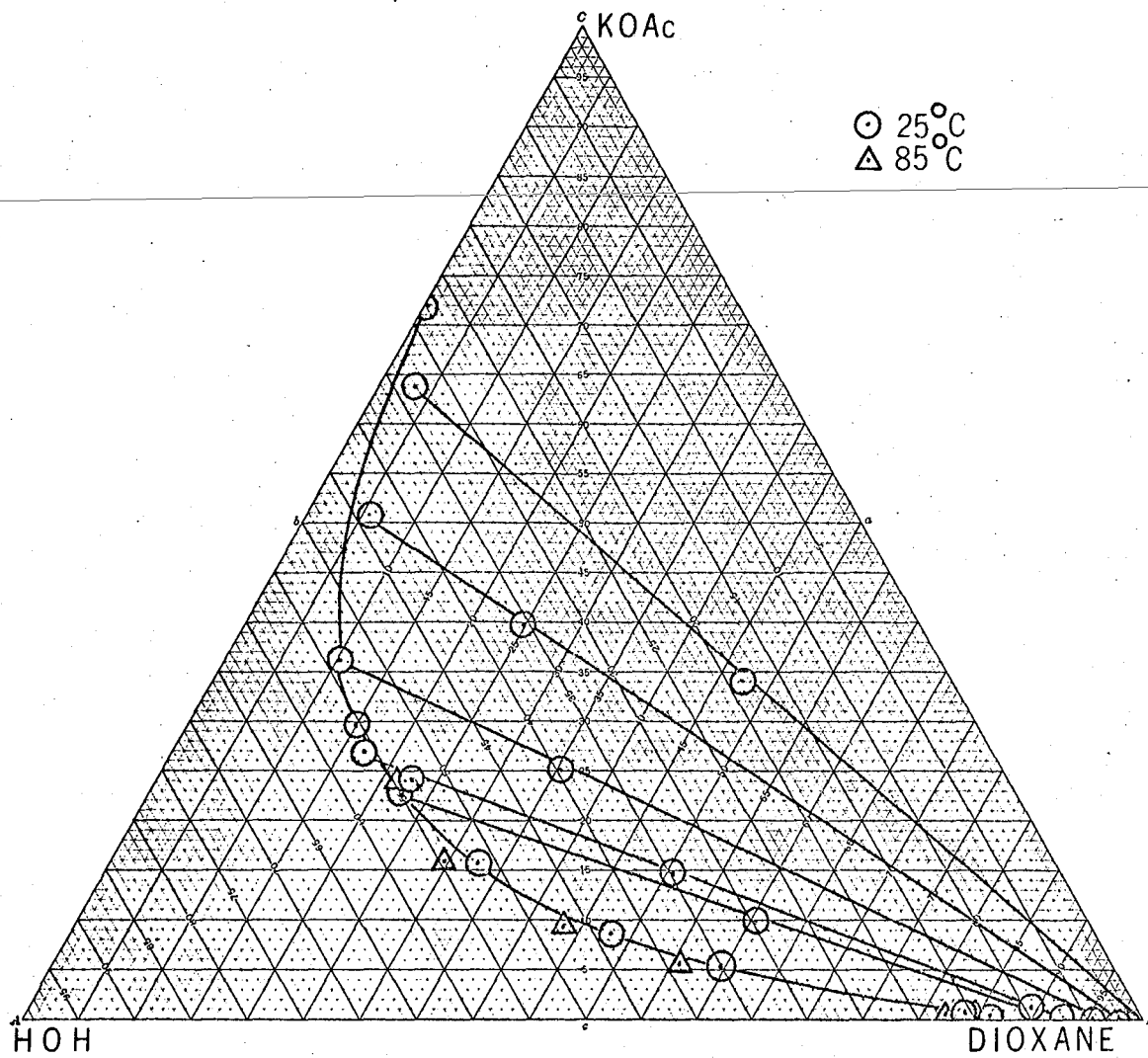


FIGURE 4

ISOTHERMS OF POTASSIUM ACETATE-WATER-DIOXANE IN WEIGHT %

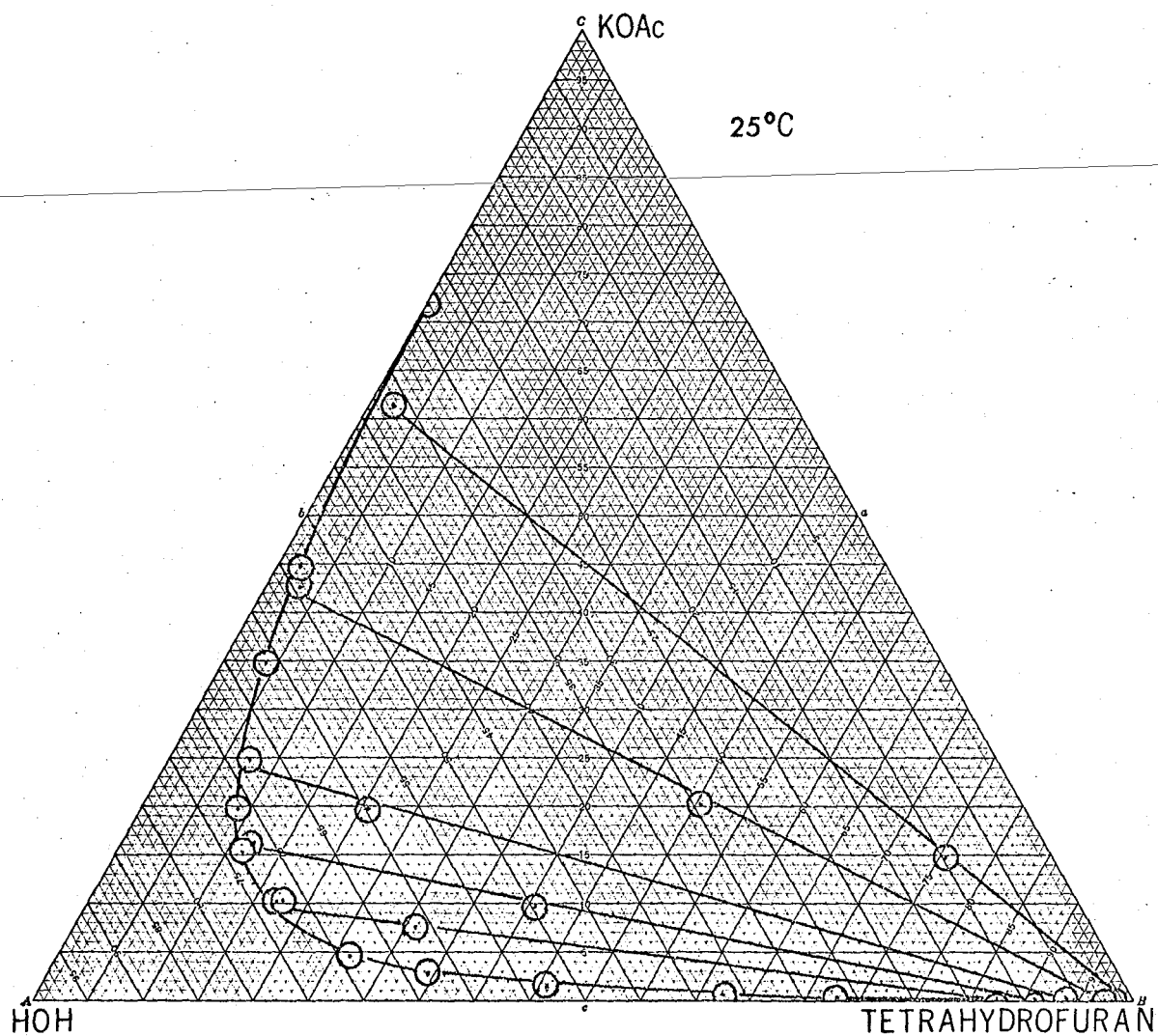


FIGURE 5

ISOTHERM OF POTASSIUM ACETATE-WATER-  
TETRAHYDROFURAN IN WEIGHT %

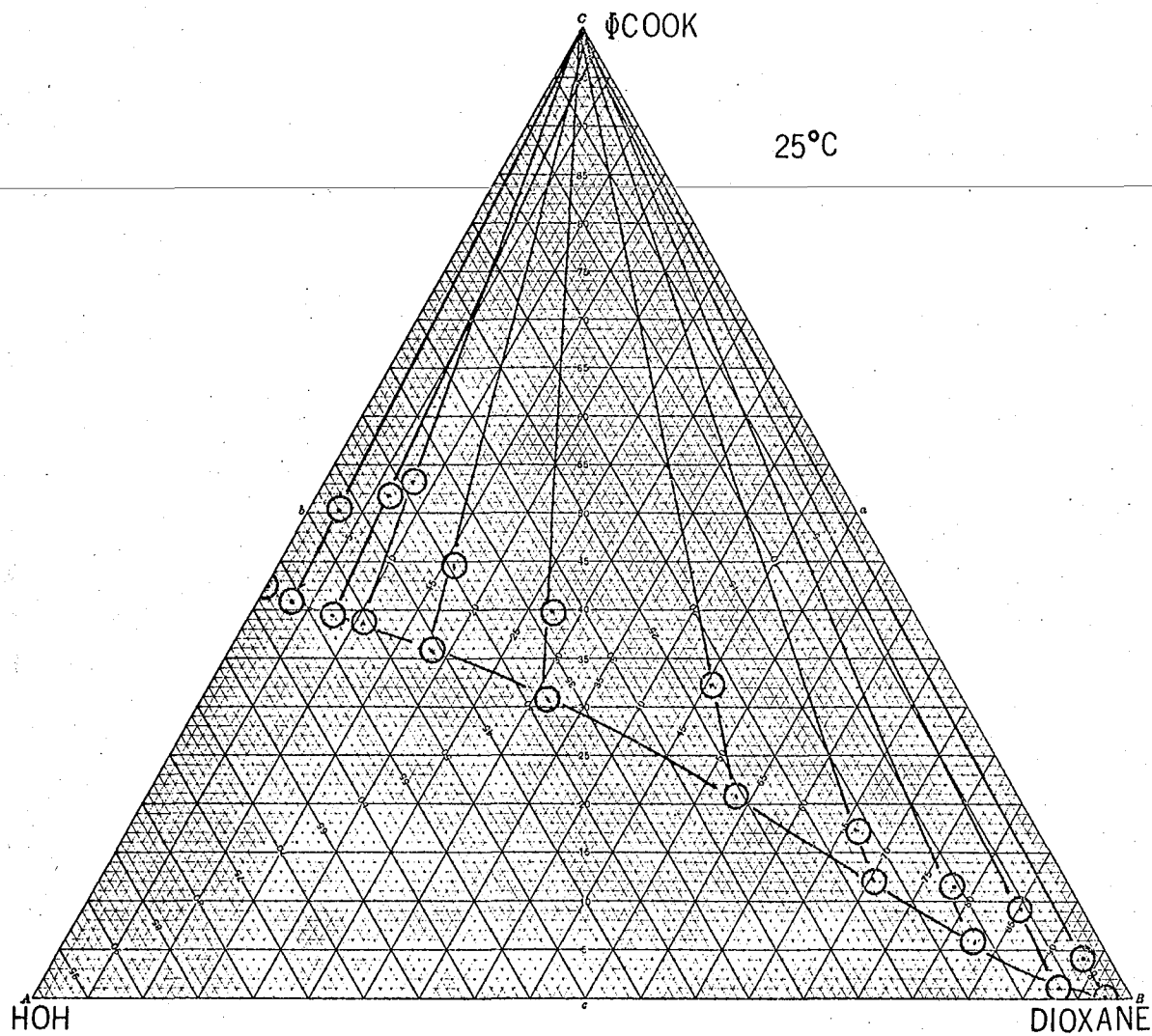


FIGURE 6

ISOTHERM OF POTASSIUM BENZOATE-WATER-DIOXANE IN WEIGHT %

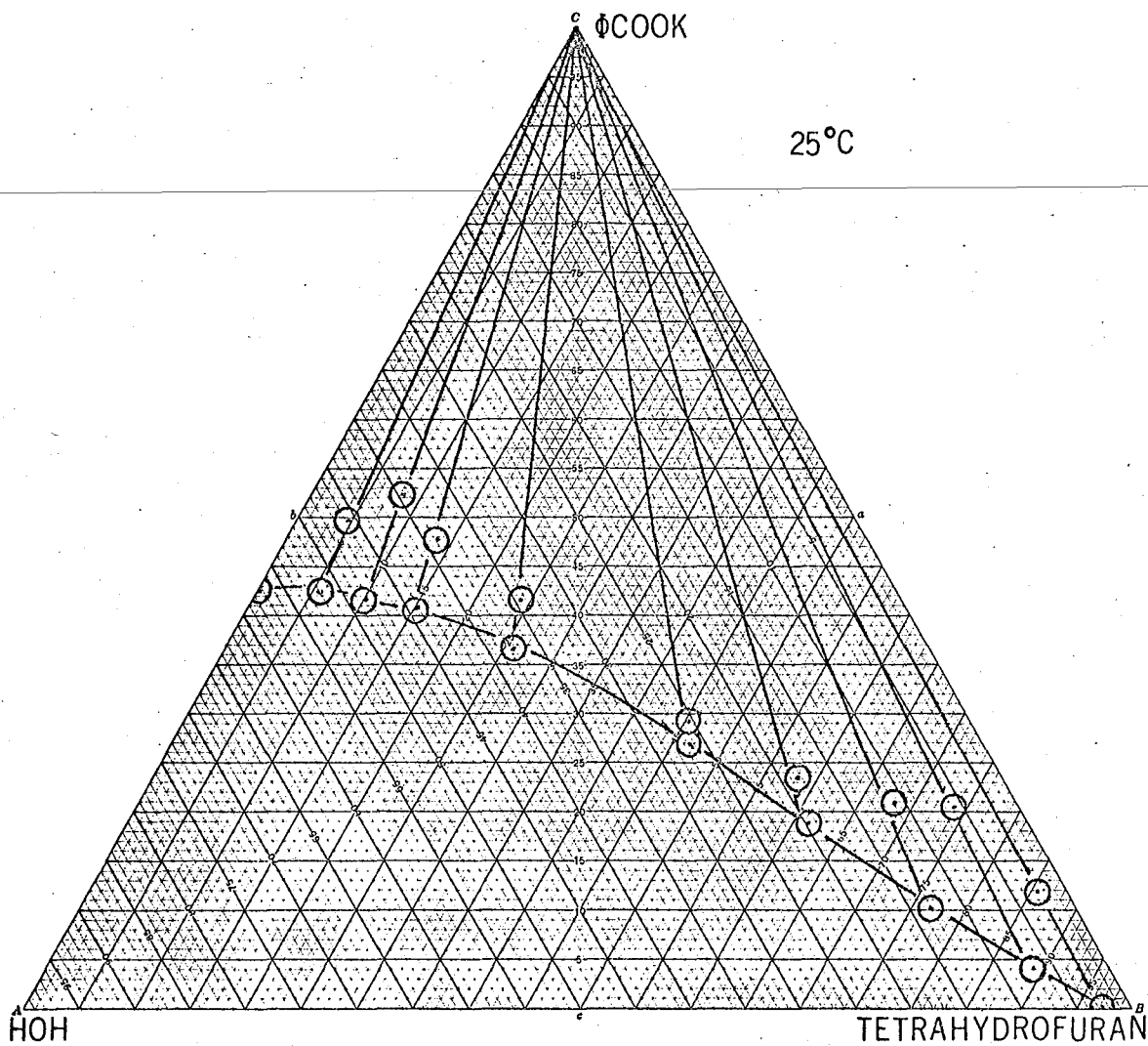


FIGURE 7

ISOTHERM OF POTASSIUM BENZOATE-WATER-  
TETRAHYDROFURAN IN WEIGHT %

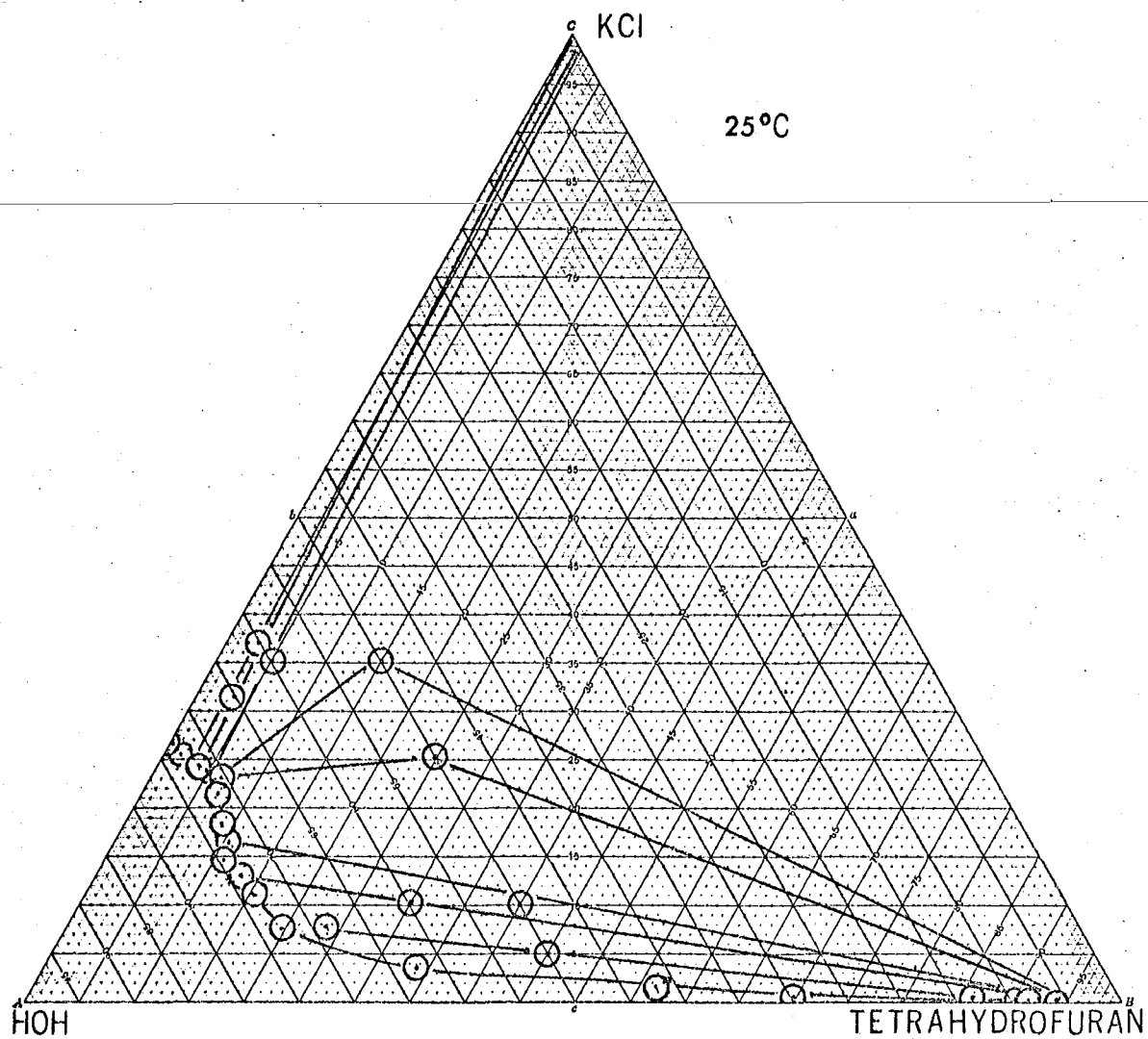


FIGURE 8

ISOTHERM OF POTASSIUM CHLORIDE-WATER-  
TETRAHYDROFURAN IN WEIGHT %

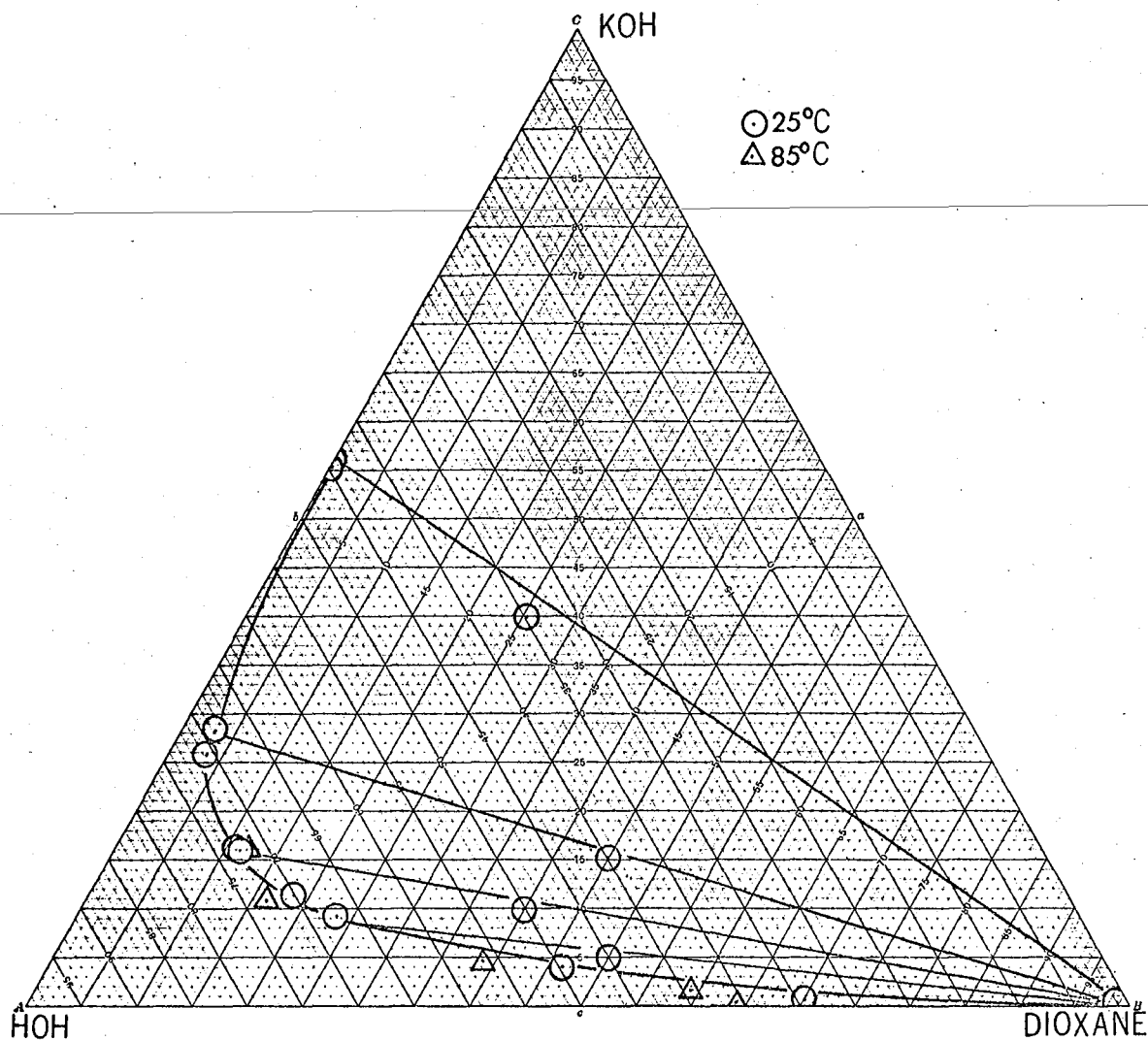


FIGURE 9

ISOTHERMS OF POTASSIUM HYDROXIDE-WATER-DIOXANE IN WEIGHT %

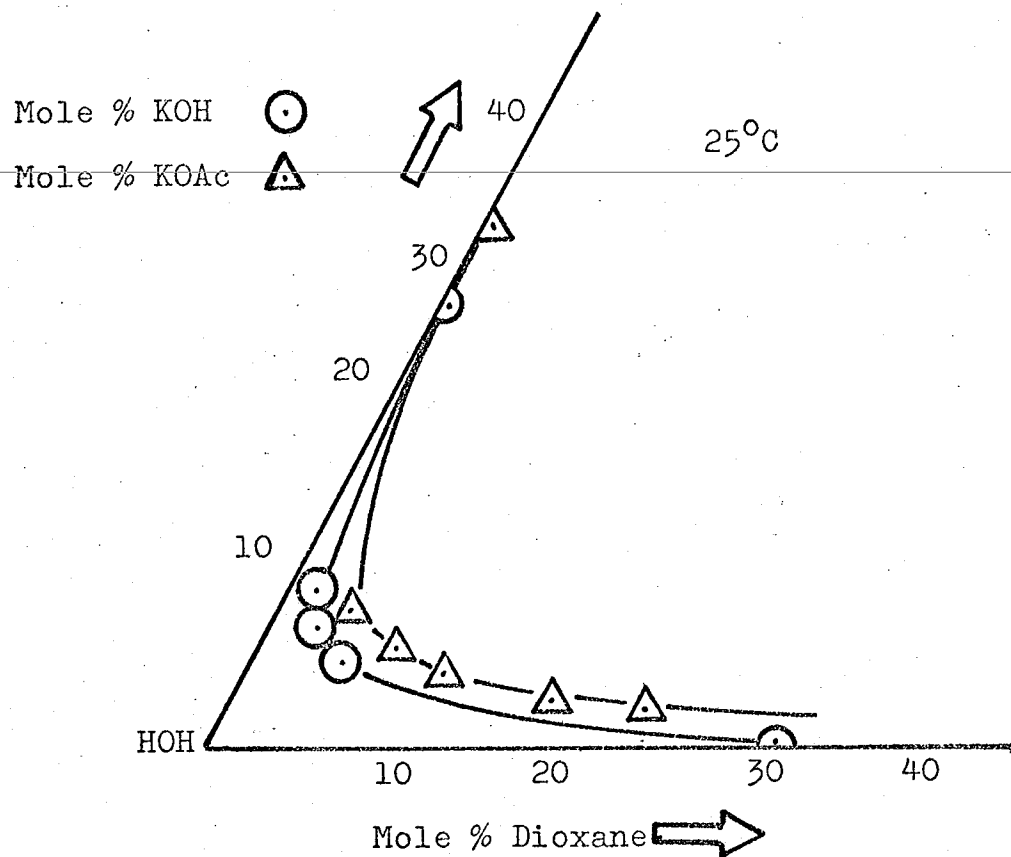


FIGURE 10

COMPARISON OF POTASSIUM HYDROXIDE WITH POTASSIUM  
ACETATE IN WATER-DIOXANE

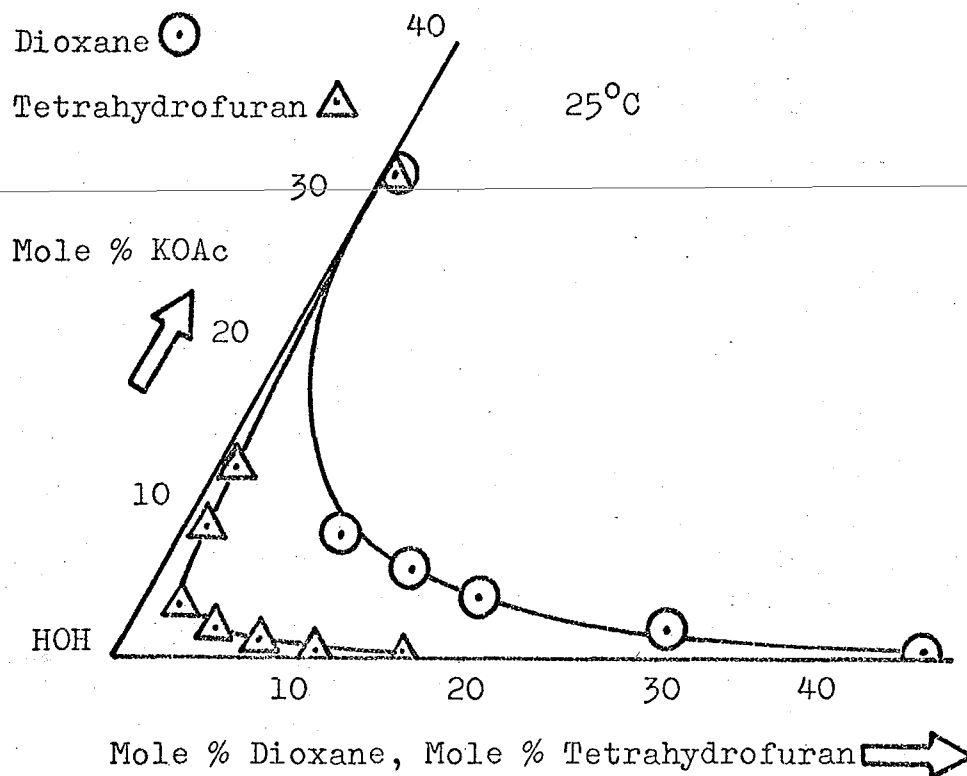


FIGURE 11

COMPARISON OF POTASSIUM ACETATE-WATER-DIOXANE  
AND POTASSIUM ACETATE-WATER-  
TETRAHYDROFURAN PLOTS



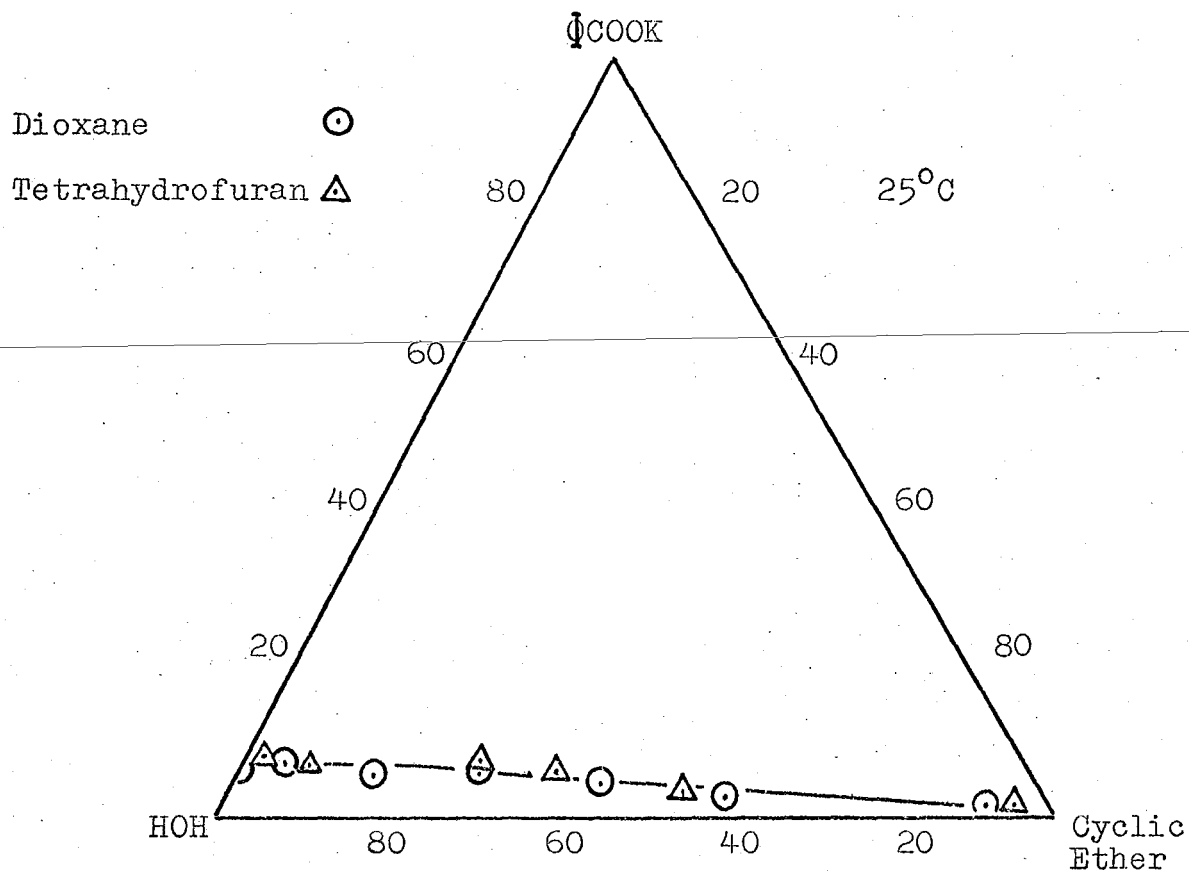


FIGURE 12

A COMPARISON OF THE SOLUBILITY CURVES OF  
 POTASSIUM BENZOATE-WATER-DIOXANE  
 AND POTASSIUM BENZOATE-WATER-  
 TETRAHYDROFURAN IN MOLE %