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Effect Of Substituents On The Distribution Coefficient Of Benzoic Acids

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EFFECT OF SUBSTITUENTS ON THE DISTRIBUTION
COEFFICIENT OF BENZOIC ACIDS

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By

Dale Timothy Lee

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in the

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I. The author wishes to express his indebtedness to Mr. R. P. Perry for the helpful suggestions and criticisms offered by him throughout the preparation of this work.

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weight of the solute is the same in both solvents, the ratio in which it distributes itself between them is constant, at constant temperature, or, in other words, Henry's law is applicable; and (b). If there are several solutes in solution, the distribution of each solute is the same as if it were present alone. This is clearly Dalton's law of partial pressures. The ratio in which the solute distributes itself between the two solvents is termed the coefficient of distribution. When the molecular weight of a solute is not the same in both solvents, the distribution coefficient is not

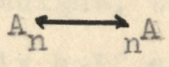
I N T R O D U C T I O N

When an aqueous solution of succinic acid is shaken with ether, the acid distributes itself between the ether and the water in such a way that the ratio between the two concentrations is always constant. It will be seen that the distribution of succinic acid between two solvents is analogous to that of a substance between the liquid and gaseous phases, and therefore, the laws governing the latter equilibrium should apply equally to the former.

(1) Nernst has shown that (a). If the molecular weight of the solute is the same in both solvents, the ratio in which it distributes itself between them is constant, at constant temperature, or, in other words, Henry's law is applicable; and (b). If there are several solutes in solution, the distribution of each solute is the same as if it were present alone. This is clearly Dalton's law of partial pressures. The ratio in which the solute distributes itself between the two solvents is termed the coefficient of distribution. When the molecular weight of a solute is not the same in both solvents, the distribution coefficient is not

constant, and conversely, if the distribution coefficient is not constant, it is inferred that the solute in the two solvents are not identical.

In assuming that a solute whose normal molecular weight is A, when shaken with two immiscible solvents, undergoes polymerization in one of them its molecular weight being A_n. We then assume the equilibrium,



and applying the law of mass action we assume,

$$\frac{C_A^n}{C_{A_n}} = K_c$$

If the molecular weight in one solvent is twice the molecular weight in the other, then n = 2 and,

$$C_1^2 / \sqrt{C_2} \text{ or } C_1 = K = \text{constant}$$

Thus, Nernst found the following concentrations of benzoic acid when it was shaken with benzene and water.

Table I

DISTRIBUTION OF BENZOIC ACID AT 20°

C ₁ Water	C ₂ Benzene	C ₁ /C ₂	C ₁ /√C ₂
0.0150	0.242	0.062	0.0305
0.0195	0.412	0.048	0.0304
0.0285	0.970	0.030	0.0293

As will be seen the values of the ratio C_1/C_2 steadily decrease, while on the other hand, the values of the ratio $(C_1)^2/C_2$ remain constant. This shows, therefore that benzoic acid has twice the normal molecular weight in benzene.

This fact is fully corroborated by direct measurements of molecular weight, the elevation of the boiling points being only half as large as expected on the assumption that the molecular weight is the sum of the atomic weights. Benzoic acid gives a normal molecular weight in alcohol and in many other solvents; and moreover benzene does not cause association or polymerization of all solutes. The phenomena are not fully understood but it seems likely that substances which give associated molecules in the gas phase (on account of special groupings in the crystal lattice, or on account of unsatisfied valencies or for other reasons) will give associated molecules also in benzene and certain inert solvents. Other solvents like water and alcohol which are themselves associated, on the other hand, appear to be able to break down the associated solute molecules.

The distribution ratio is identical with the ratio of solubilities in the two solvents when the solute is very sparingly soluble. Still in most cases the

saturated solutions are so concentrated and so far from ideal that the mass law no longer holds. Under these conditions the coefficient of distribution changes with the concentration and the distribution ratio in dilute solutions may differ largely from the solubility ratio.

A search through the literature revealed the following facts concerning distribution and polymerization.

(2)

Shikata, in the study of the partition of acetic acid between organic solvent and water, used the following procedure: By letting C_{nH} be the concentration of uni-molecular alcohol in H_2O and C_s the concentration in the other layer; the partition coefficient, (K), was given as $C_s = KC_{nH}$ (I); K remains constant, at constant temperature, regardless of the concentration. By representing molecular association as C_B the equilibrium constant. $K = (C_3)^2 / \frac{1}{2}(C_B C_3)$ II. In the combination of I and II, $K = (kC_{nH})^2 / \frac{1}{2}(C_s - kC_{nH})$ III and $k = \frac{1}{4}C_{nH}(\sqrt{K^2 + 8KC_B} - K)$ IV are obtained. From the experimental results

$k = \frac{[(C_{nH.1}^2 \cdot C_{B.2})]}{(C_{nH.1} C_{nH.2})(C_{nH.1} - C_{nH.2})}$ or a linear formula VI is obtained thus:

$C_B = C_5 + (2C_5^2 / K) = kC_{nH} + (2k^2 C_{nH}^2 / K)$. Therefore,

$C_B / C_{nH} = k + (2k^2 / K) \times C_{nH}$, $a = C_B / C_{nH}$, $b = 2k^2 / K$,

$a = k + bC_{nH}$ VI. When the experimental value of C_{nH}

is plotted against C_B/C_{nH} , (VI) can be expressed in a straight line; therefore, the values of k and K can be attained from the graph or by the least square method. The degree of association of $CCl_4 > C_6H_6$ and dissociation increases with the temperature while $CHCl_3$ is reciprocal. The heat of dissociation calculated from the association equilibrium are C_6H_6 , 7302 calories, CCl_4 11,025 calories, and $CHCl_3$, 8840 calories.

In the study of the influence of solutes on the partition of acetic acid between organic solvent and water he found in the preceding data that the addition of solutes increased the movement of alcohol in water to the organic solvent. In general, this tendency is greater with salts of alkaline earth metals than with alkali metals. Among the salts of metals of the same group, the smaller the atomic weights of the cation the greater the effect among the anions $SO_4 -- > Cl - > AcO -$. The relation expressed in equation (VI) in the preceding data does not change on the addition of these salts. The effect of concentrations of HCl and HNO_3 are parallel with the concentration; H_2SO_4 differs slightly from HCl , while $NaCl$ increases in effect rapidly with an increase in temperature. The effect is attributed to the formation of hydrates. For hydrate formation, chlorides of magnesium and calcium $>$ sulfates $>$ nitrates $>$ acetates. Among the salts of the same atomic group, hydration is strongest when the atomic weight of the metal is the smallest.

Archibald (3), in his study of the distribution of acid between water and several immiscible solvents, de-

terminated the distribution ratios at 25^o of the six straight chain members of the saturated monocarboxylic acid series from formic acid to caproic acid between water and the following solvents: ethyl methyl ketone, tertiary amyl alcohol, secondary butyl alcohol, normal butyl alcohol and normal amyl alcohol. Data was also included from the literature for ratios between ethyl ether and water and between isopropyl ether and water. Since the distribution ratios change slightly with the concentration of the acid, the values of the ratios for ethyl ether were estimated for an acid concentration of about 0.001 M in the water layer. The values for isopropyl ether and water were obtained by using weighed means from three papers cited for an average acid concentration of both layers of about 0.05 M.

Blank titrations were made on all solvents in equilibrium with distilled water at 25^oC. These titrations showed us appreciable acid in either the water or any of the solvents. The acids used were high grade commercial C. P. products. The solvent, water and acid were mixed in a flask and allowed to remain, with frequent shaking, in a thermostat at 25.00 \pm .01^o for several hours. Samples of each layer were pipetted out and titrated in duplicate against standardized 0.1 N. sodium hydroxide, using phenolphthalein as indicator. These samples were 25 cc. in all

cases except the higher concentrations of formic, acetic and butyric acids, of which 10 cc. samples were used.

This work was undertaken for its bearing on the possibility of separating sterols from vitamins by forming some ester of the sterol, such as the gluconate, which might be slightly soluble in water, and fractionating the mixture in a column which gives multiple distribution between two immiscible solvents. This work is also of interest in connection with the Dakin process for separating amino acids. This process consists in extracting a water solution of the mixed amino acid with normal butyl alcohol or other solvents. The strongly ionized amino acids remain in the water layer, while the slightly ionized acids are extracted.

In part II of his study he considered the distribution of hydrochloric, nitric, sulfuric, and perchloric acid between water and some of the non-aqueous solvents used in part I. Distribution of these acids was determined in three concentrations, the average concentration for both layers being about 0.05, 0.25, and 1.25 N. The layers were approximately equal in volume. The experimental method is identical with that used for the monocarboxylic acids.

The purpose of this research was to determine quantitatively which acid would be most suitable for acidifying a water solution, one component of which was to be extracted with one of the solvents mentioned above. Since it was necessary to extract with very large amounts

of solvent, many times it was imperative that the acid be very insoluble in the solvent in order that the solution remain acid until the end of the extraction process.

He concluded that in any solvent the order of the curves from the line of unit distribution ratio is H.ClO_4 , HNO_3 , HCl , H_2SO_4 , which follows the Hofmeister series for the precipitation of proteins, the sulfate ion being the most efficient. The series is also the same as that found by Randall and Farley (4), for the salting out effect, rather than the strength of acids series which give the order HNO_3 , HCl , H_2SO_4 , HClO_4 where perchloric acid is the strongest.

Smith and Norton (5), have studied the distribution ratios and association of carboxylic acids. They have determined the distribution of H.COOH , ACOH , butyl alcohol, caprylic, lauric, palmitic, oleic, and 50% oleic - 50% linoleic acids at 0°C . between 2,2,4, trimethylpentane and CH_3OH and also the distribution of lauric, oleic, maleic, fumaric and the phthalic acids between 2,2,4 trimethylpentane and CH_3CN .

It was indicated that carboxyl groups tend to associate with each other in pairs and this tendency was not destroyed by esterification. This "self-association" may be inhibited by the presence of enough of a somewhat basic solvent.

Two carboxyls close together in the same molecule tend toward "self association" with each other rather than with carboxyls from other molecules. The tenacity of Japan wax and of cellulose esters is explained by these theories. The author gives also values of the distribution of fatty acids between iso-octane and methyl cyanide, and between iso-octane and methanol.

Bronsted and Warming (6), in their study of the distribution of colloid particles between two immiscible solvents, found that the theoretically anticipated one-sidedness in the partition of colloid particles between two immiscible solvents was varified for the colloids, As_2S_3 and $Cr(OH)_3$, in the neighborhood of the critical solvent temperature of water - butyl alcohol - ethyl alcohol mixtures. For small differences in temperatures the logarithms of the partition coefficient is proportional to the square root of the distance from the critical solvent temperature.

Bodansky and Meigs (7), determined the distribution ratio of some fatty acids and their halogen derivatives between water and olive oil at 25° and 37.5° . Some of the values of the true partition coefficient was calculated, these, averaged are given in parenthesis for 25° and 37.5° , respectively:

HOAC, $\text{CH}_2\text{ClCO}_2\text{H}$ (0.08), $\text{CH}_2\text{BrCO}_2\text{H}$, $\text{CH}_3\text{ICO}_2\text{H}$, $\text{CHCl}_2\text{CO}_2\text{H}$,
 $\text{CCl}_3\text{CO}_2\text{H}$, EtCO_2H (0.16, 0.26), $\text{CH}_2\text{ClCH}_2\text{CO}_2$ (0.31),
 $\text{MeCHBrCO}_2\text{H}$ (0.66), $\text{CH}_2\text{BrCH}_2\text{CO}_2\text{H}$ (0.46), PrCO_2H (0.60, 0.66),
 $\text{iso-PrCO}_2\text{H}$ (0.74, 0.82), $\text{EtCHBrCO}_2\text{H}$ (1.38), BuCO_2H (3.04, 3.03),
 $\text{iso-BuCO}_2\text{H}$ (1.9, 1.8), $\text{PrCHBrCO}_2\text{H}$, and AMCO_2H .

Glossfeld and Miermeister (8), examined the behaviour of caprylic, caproic, valeric, isovaleric and benzoic acid in water and petroleum ether and showed that the partition of the five acids mentioned for different acid concentrations corresponds to $k = C_1/\sqrt{C_2}$. For shaking the aqueous solution with an equal volume of petroleum ether, the following formulas hold in which C_0 represents the initial concentration and C_1 the final concentration in the aqueous phase. (I) Expressed as 0.1 N acid per 25 cc. we have: (a) caproic acid, $C_1 = - 0.15 \sqrt{0.30 / C_0}$; (b) valeric acid, $C_1 = - 2.42 \sqrt{4.84 C_0 / 5.86}$; (c) isovaleric acid, $C_1 = - 3.54 \sqrt{7.08 C_0 / 12.53}$. (II) Expressed as 0.002 N acid per 25 cc.; (a) caprylic acid, $C_1 = - 0.09 \sqrt{0.185 C_0 / 0.0009}$; (b) benzoic acid, $C_1 = - 55.65 \sqrt{110.3 C_0 / 3097}$. A table was given which showed the percentage decrease in acidity after shaking 0.001 - 1 N solution of the acid with an equal volume of petroleum ether.

Daniels and Lyons (9), in their study of the physical

properties of solutions of certain phenyl-substituted acids in relation to their bactericidal power, determined the solubilities in H_2O , distribution between H_2O and cottonseed oil and adsorption on activated carbon, and also the relative viscosities, surface tensions and p^H of dilute solutions for the series: phenylacetic, β -phenylpropionic, γ -phenylbutyric, δ -phenylvaleric, and ϵ -phenylcaproic acids. (The corresponding data for benzol alcohol are quite different). Bactericidal action in the series increases with the length of the chain and closely parallels, the oil-water distribution and carbon adsorption curves. The p^H and viscosities of the solutions varied too little to be considered.

(10)

Florence , has studied the distribution of acetophenone and some of its derivatives between olive oil and water.

(11)

Angelescu and Dutchievici , in their study of the hydration of several electrolytes, determined by the distribution of an aliphatic acid between benzene and water, showed the distribution of butyric acid between benzene and water and normal aqueous solutions of various electrolytes. For the equations:

$C_{H_2O} = K C_{Benzene}^P$, it was found that $K = 0.739$ and $P = 0.615$, at 20° , for a concentration in g/100 cc. of solution; between 6.49 and 32.61 in benzene and 2.39 and

6.39 in water. The decrease in solubility in aqueous solutions of electrolytes was attributed to the immobilization of N mols of water by each mol of electrolyte. The value of N was found to be for: NaCl, 18.0; NaBr, 16.4; NaI, 10.6; NaNO₃, 11.1; KCl, 16.3; KBr, 11.5; KI, 8.1; and KNO₃, 46.0. In general, the value of N decreased slightly as the concentration of butyric acid increased. The results are in fair agreement with those of other investigators using different methods.

(12)

Kolosorskii and Mezhenin, investigated the distribution of formic, acetic, and propionic acids between water and toluene.

PURPOSE OF THIS WORK

A review of the literature reveals no work in which there was some effort made to show the effect of substituents on the distribution coefficients of benzoic acids between water and benzene. The author decided to prepare and study certain or some typical benzoic acids. The author wished to determine further whether or not substituents influenced the polymerization of benzoic acids in benzene. The author hoped to collect data on substituted benzoic acids and determine if the substituted benzoic acids undergo polymerization in benzene. He also wished to determine if the position of the group and temperature are factors influencing polymerization and the distribution of benzoic acids between water and benzene.

EXPERIMENTAL PART

For this determination benzoic acid and the following substituted benzoic acids were used: o-amino benzoic, o-chlor benzoic, salicylic, acetyl-salicylic, phthalic, o-nitro benzoic, and m-nitro benzoic acids. The majority of these acids were either taken from stock or prepared by standard methods. The m-nitro benzoic acid, however, was prepared by direct substitution of the nitro group into the benzene ring. In this preparation 10.9 grams of benzoic acid were added in small portions to 8.5 cc of fuming nitric acid and kept at 5°C. When all the benzoic acid had been added the mixture was poured into a solution of ice and water. The nitro compound was precipitated out, filtered by suction, and washed several times with water. When the product was dry, it was recrystallized from alcohol. The purified product melted at 140°C. All of the benzoic acids were recrystallized several times from suitable solvents until they gave sharp melting points. The compounds were then dried and sealed in sample bottles until they were used in the determination.

For the determination of the distribution coefficient the necessary amounts of acids to prepare a 1, 2, and 3 percent solution were placed into 125 cc

Florence flasks. The acid was then treated with 25 cc. portions of distilled water and 25 cc. portions of benzene. The flasks were then stoppered tightly, shaken vigorously, and placed in a thermostat at the desired temperature for 30 minutes. At the end of a 30 minute period 10 cc. portions of the benzene and water layers were withdrawn by means of a pipette and titrated separately against a standard one-tenth normal sodium-hydroxide solution, using phenolphthalein as indicator. From the respective acid titres and the volume of sodium-hydroxide used the concentration of the acid in the benzene and water layers was calculated, expressing the final results in terms of mols of acid per 1000 cc. of solution. The following tables give the results obtained in each determination.

I. Tables II, III, and IV of benzoic acid after investigation show distinctly that the acid had undergone polymerization, as had been stated in the literature. It also showed a gradual decrease in the distribution coefficient as the temperature was lowered. The temperature had little affect on the polymerization constant.

II. Tables V, VI, and VII of o-amino benzoic acid after investigation show neither distribution nor polymerization. It was clearly seen that the amino group must have caused a change. The change is, however, more toward that of polymerization.

III. Tables VIII, IX and X of o-chlor benzoic acid after investigation show that the acid had little

effect on the distribution coefficient or the polymerization constant. However, it did cause an increase in the concentration at 20° and 15°. The lowest concentration throughout the three temperatures was in the 2% solution.

IV. Tables XI, XII, and XIII show that the salicylic acid tends toward distribution rather than polymerization. There was an increase in concentration as shown in table XII and XIII at 20° and 15°. This was probably due to the fact that the acid becomes less soluble in the benzene layer. At the lower temperatures there was an increase in the values of the distribution coefficient.

V. Tables XIV, XV, and XVI seem to show neither distribution nor polymerization for phthalic acid. The acid was very insoluble in the benzene layer and the temperature had no affect upon the solubility.

VI. Tables XVII, XVIII, and XIX show that acetyl salicylic acid tended toward distribution rather than polymerization. Table XIV show more of a constant than the others. This was due to the temperature at which the acid was less soluble in the benzene layer. The distribution coefficient increased as the temperature decreased.

VII. Tables XX, XXI, and XVII of o-nitro benzoic acid after investigation show a greater tendency toward distribution. The distribution coefficient decreased with the temperature. However, there was little change

THESE DATA ARE EXPRESSED IN MOLES PER 1000 G. OF SOLVENTS in the distribution coefficient for the three concentrations at definite temperature conditions. The concentrations of 2 and 3% remained the same at the various temperatures.

VIII. Tables XXIII, XXIV, and XXV show that the m-nitro benzoic acid tended toward polymerization. The decrease in concentration observed was probably due to the position of the nitro group.

In no case did a substituted benzoic acid tend wholly toward polymerization in benzene.

TABLE III.
DISTRIBUTION OF BENZOIC ACID AT 30°

Percent	C ₁ Water	C ₂ Benzene	C ₁ /C ₂	C ₁ /√C ₂
1	.00962	.08409	.1180	.00138
2	.01380	.16800	.0880	.00113
3	.01760	.27000	.0550	.00114

TABLE IV.
DISTRIBUTION OF BENZOIC ACID AT 15°

Percent	C ₁ Water	C ₂ Benzene	C ₁ /C ₂	C ₁ /√C ₂
1	.00904	.0848	.1060	.00096

THESE DATA ARE EXPRESSED IN MOLS PER 1000 cc. OF SOLUTION

TABLE II.

DISTRIBUTION OF BENZOIC ACID AT 25°

Percent	C ₁ Water	C ₂ Benzene	C ₁ /C ₂	C ₁ /√C ₂
1	.01070	.08870	.1206	.00129
2	.01380	.16800	.0886	.00115
3	.01770	.26100	.0678	.00120

TABLE III.

DISTRIBUTION OF BENZOIC ACID AT 20°

Percent	C ₁ Water	C ₂ Benzene	C ₁ /C ₂	C ₁ /√C ₂
1	.00962	.08409	.1140	.00110
2	.01380	.16800	.0886	.00113
3	.01760	.27000	.0650	.00114

TABLE IV.

DISTRIBUTION OF BENZOIC ACID AT 15°

Percent	C ₁ Water	C ₂ Benzene	C ₁ /C ₂	C ₁ /√C ₂
1	.00904	.0848	.1060	.00096
2	.01300	.1640	.0792	.00102
3	.01700	.2640	.0643	.00110

THESE DATA ARE EXPRESSED IN MOLS PER 1000 cc. OF SOLUTION

TABLE V.

DISTRIBUTION OF O-AMINO BENZOIC ACID AT 25°

Percent	C ₁ Water	C ₂ Benzene	C ₁ /C ₂	C ₁ /√C ₂
1	.0297	.0474	.626	.0188
2	.0480	.0936	.512	.0246
3	.0511	.1160	.440	.0225

TABLE VI.

DISTRIBUTION OF O-AMINO BENZOIC ACID AT 20°

Percent	C ₁ Water	C ₂ Benzene	C ₁ /C ₂	C ₁ /√C ₂
1	.0292	.0436	.669	.0195
2	.0448	.0944	.474	.0211
3	.0468	.0958	.487	.0228

TABLE VII.

DISTRIBUTION OF O-AMINO BENZOIC ACID AT 15°

Percent	C ₁ Water	C ₂ Benzene	C ₁ /C ₂	C ₁ /√C ₂
1	.0303	.0461	.657	.0199
2	.0450	.0916	.492	.0221
3	.0447	.0758	.589	.0263

THESE DATA ARE EXPRESSED IN MOLLS PER 1000 cc. OF SOLUTION

TABLE VIII.

DISTRIBUTION OF O-CHLOR BENZOIC ACID AT 25°

Percent	C ₁ Water	C ₂ Benzene	C ₁ /C ₂	C ₁ /√C ₂
1	.0090	.0583	.154	.00138
2	.0144	.1190	.121	.00174
3	.0151	.1160	.130	.00196

TABLE IX.

DISTRIBUTION OF O-CHLOR BENZOIC ACID AT 20°

Percent	C ₁ Water	C ₂ Benzene	C ₁ /C ₂	C ₁ /√C ₂
1	.0094	.0588	.159	.00150
2	.0149	.1200	.124	.00185
3	.0171	.0952	.179	.00300

TABLE X.

DISTRIBUTION OF O-CHLOR BENZOIC ACID AT 15°

Percent	C ₁ Water	C ₂ Benzene	C ₁ /C ₂	C ₁ /√C ₂
1	.0101	.0583	.173	.00174
2	.0133	.0914	.149	.00193
3	.0139	.0775	.166	.00249

THESE DATA ARE EXPRESSED IN MOLS PER 1000 cc. OF SOLUTION

TABLE XI.

DISTRIBUTION OF SALICYLIC ACID AT 25°

Percent	C ₁ Water	C ₂ Benzene	C ₁ /C ₂	C ₁ /√C ₂
1	.0169	.0618	.273	.00447
2	.0186	.0691	.267	.00500
3	.0181	.0681	.268	.00481

TABLE XII.

DISTRIBUTION OF SALICYLIC ACID AT 20°

Percent	C ₁ Water	C ₂ Benzene	C ₁ /C ₂	C ₁ /√C ₂
1	.0169	.0621	.272	.00444
2	.0169	.0553	.305	.00498
3	.0169	.0548	.308	.00502

TABLE XIII.

DISTRIBUTION OF SALICYLIC ACID AT 15°

Percent	C ₁ Water	C ₂ Benzene	C ₁ /C ₂	C ₁ /√C ₂
1	.01510	.0601	.251	.00379
2	.01490	.0452	.329	.00469
3	.01518	.0479	.317	.00476

THESE DATA ARE EXPRESSED IN MOLS PER 1000 cc. OF SOLUTION

TABLE XIV.

DISTRIBUTION OF PHTHALIC ACID AT 25°

Percent	C ₁ Water	C ₂ Benzene	C ₁ /C ₂	C ₁ /√C ₂
1	.03398	.00103	32.990	1.131
2	.04320	.00103	41.941	1.811
3	.04520	.00103	43.883	1.983

TABLE XV.

DISTRIBUTION OF PHTHALIC ACID AT 20°

Percent	C ₁ Water	C ₂ Benzene	C ₁ /C ₂	C ₁ /√C ₂
1	.03672	.00103	35.699	1.309
2	.04428	.00103	42.990	1.903
3	.04480	.00103	43.495	1.948

TABLE XVI.

DISTRIBUTION OF PHTHALIC ACID AT 15°

Percent	C ₁ Water	C ₂ Benzene	C ₁ /C ₂	C ₁ /√C ₂
1	.03038	.00103	29.495	.986
2	.04320	.00103	41.941	1.811
3	.04320	.00103	41.941	1.811

THESE DATA ARE EXPRESSED IN MOLS PER 1000 cc. OF SOLUTION

TABLE XVII.

DISTRIBUTION OF ACETYL SALICYLIC ACID AT 25°

Percent	C ₁ Water	C ₂ Benzene	C ₁ /C ₂	C ₁ /√C ₂
1	.0228	.0270	.844	.0193
2	.0248	.0290	.855	.0212
3	.0248	.0290	.855	.0212

TABLE XVIII.

DISTRIBUTION OF ACETYL SALICYLIC ACID AT 20°

Percent	C ₁ Water	C ₂ Benzene	C ₁ /C ₂	C ₁ /√C ₂
1	.0228	.0238	.958	.0214
2	.0238	.0228	1.045	.0248
3	.0238	.0238	1.000	.0238

TABLE XIX.

DISTRIBUTION OF ACETYL SALICYLIC ACID AT 15°

Percent	C ₁ Water	C ₂ Benzene	C ₁ /C ₂	C ₁ /√C ₂
1	.0218	.02060	1.058	.0230
2	.0218	.01972	1.105	.0240
3	.0228	.01972	1.156	.0258

THESE DATA ARE EXPRESSED IN MOLLS PER 1000 cc. OF SOLUTION

TABLE XX.

DISTRIBUTION OF O-NITRO BENZOIC ACID AT 25°

Percent	C ₁ Water	C ₂ Benzene	C ₁ /C ₂	C ₁ /√C ₂
1	.04054	.0186	2.125	.0882
2	.04560	.0206	2.211	.1009
3	.04560	.0206	2.211	.1009

TABLE XXI.

DISTRIBUTION OF O-NITRO BENZOIC ACID AT 20°

Percent	C ₁ Water	C ₂ Benzene	C ₁ /C ₂	C ₁ /√C ₂
1	.03638	.01662	2.182	.0790
2	.04360	.01646	2.650	.1150
3	.04360	.01646	2.650	.1150

TABLE XXII.

DISTRIBUTION OF O-NITRO BENZOIC ACID AT 15°

Percent	C ₁ Water	C ₂ Benzene	C ₁ /C ₂	C ₁ /√C ₂
1	.03324	.01363	2.438	.0810
2	.03846	.01363	2.821	.1085
3	.03846	.01363	2.821	.1085

THESE DATA ARE EXPRESSED IN MOLS PER 1000 cc. OF SOLUTION

TABLE XXIII.

DISTRIBUTION OF M-NITRO BENZOIC ACID AT 25°

Percent	C ₁ Water	C ₂ Benzene	C ₁ /C ₂	C ₁ /√C ₂
1	.01132	.0602	.1880	.00212
2	.01662	.1132	.1468	.00244
3	.01662	.1280	.1298	.00215

TABLE XXIV.

DISTRIBUTION OF M-NITRO BENZOIC ACID AT 20°

Percent	C ₁ Water	C ₂ Benzene	C ₁ /C ₂	C ₁ /√C ₂
1	.01132	.0602	.1880	.00212
2	.01662	.1139	.1459	.00242
3	.01662	.1164	.1427	.00239

TABLE XXV.

DISTRIBUTION OF M-NITRO BENZOIC ACID AT 15°

Percent	C ₁ Water	C ₂ Benzene	C ₁ /C ₂	C ₁ /√C ₂
1	.01038	.05196	.1997	.00207
2	.01247	.08316	.1499	.00186
3	.01662	.11640	.1427	.00239

FIGURE 1.

Figure 1 represents the plotted values of the distribution of benzoic acid between water and benzene.

Figure 2 represents the plotted values of the distribution of salicylic acid between water and benzene.

Comparing the two graphs, there is evidently no indication of polymerization of the salicylic acid in benzene.

This is apparently true of all of the substituted benzoic acids examined in this study.

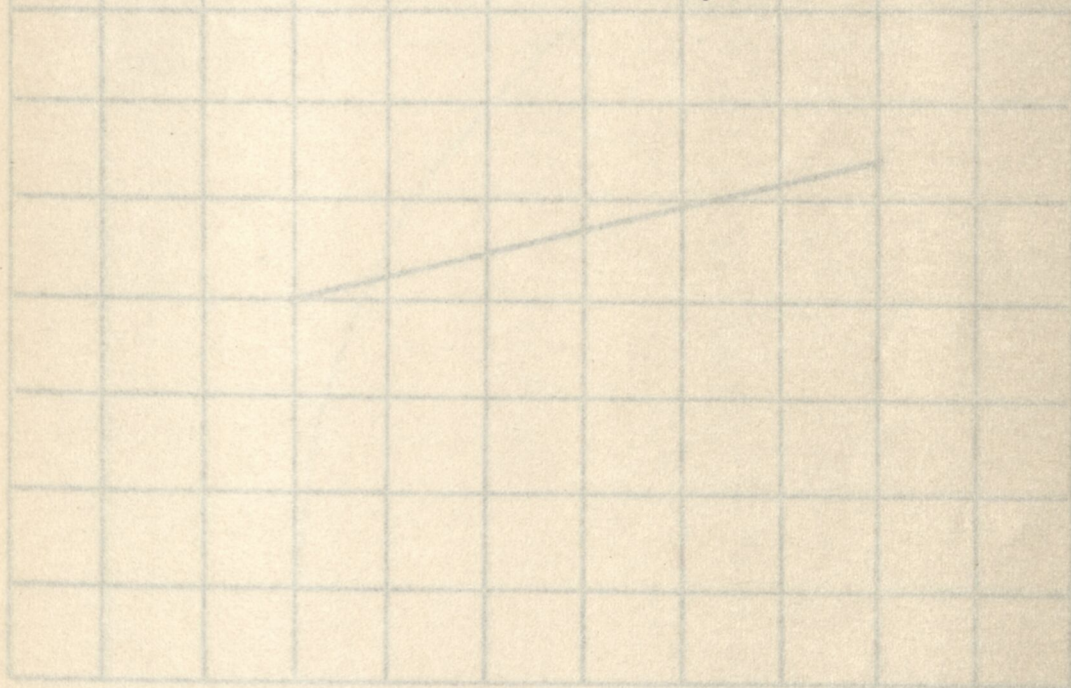
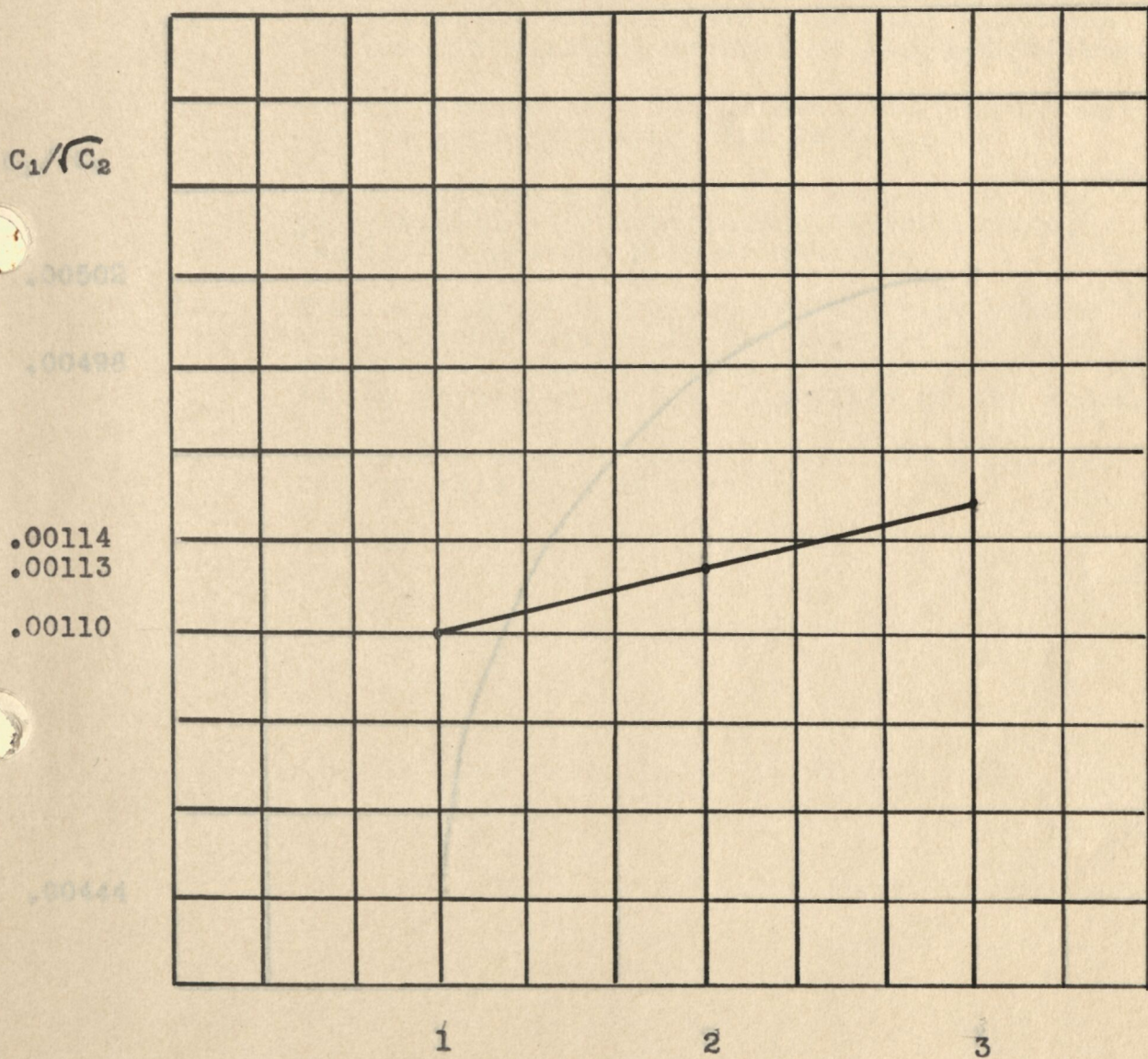


FIGURE 1.

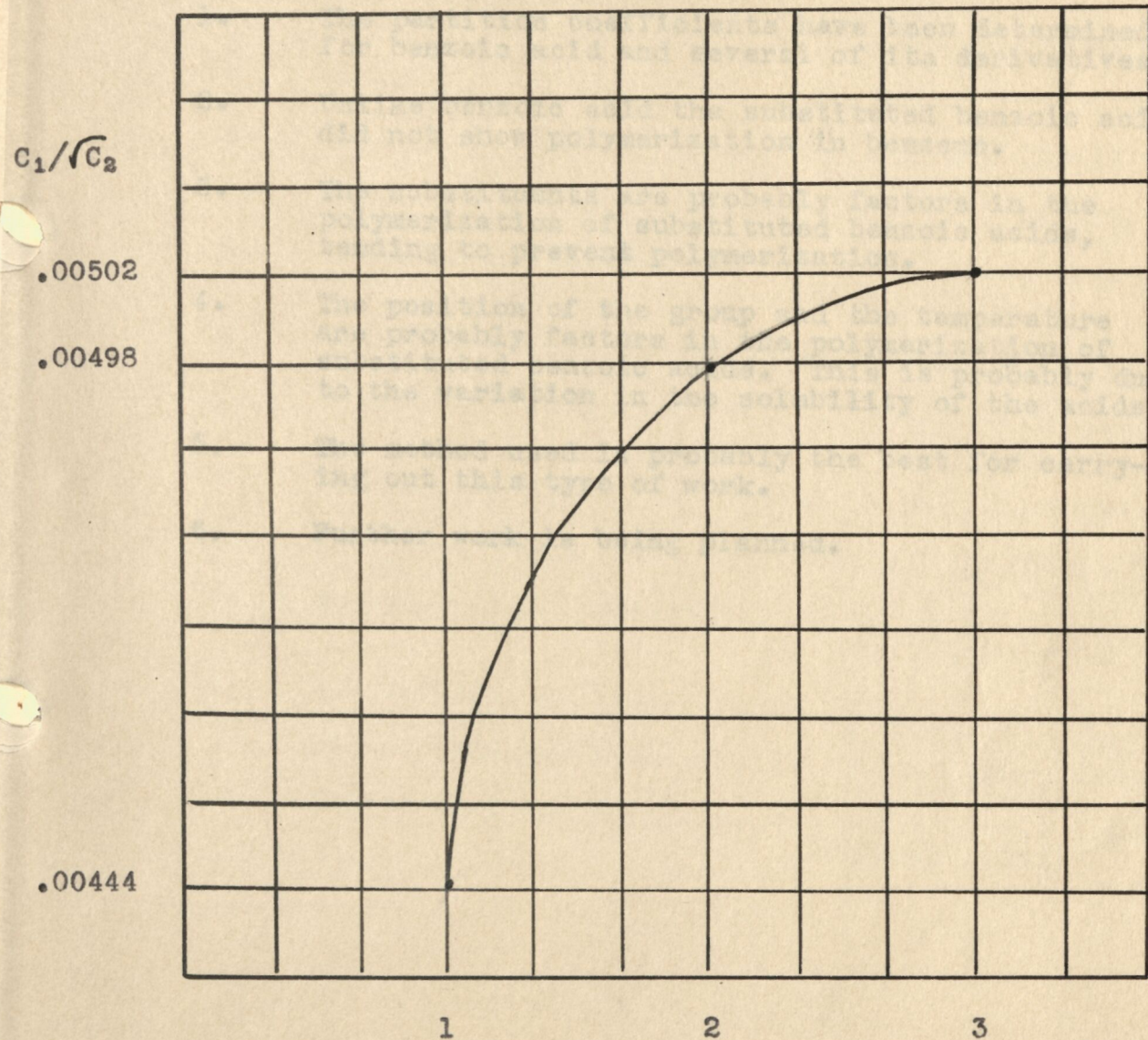
BENZOIC ACID AT 20°



CONCENTRATION IN PERCENT

FIGURE 2.

SALICYLIC ACID AT 20°



CONCENTRATION IN PERCENT

SUMMARY AND CONCLUSION

1. The partition coefficients have been determined for benzoic acid and several of its derivatives.
2. Unlike benzoic acid the substituted benzoic acids did not show polymerization in benzene.
3. The substituents are probably factors in the polymerization of substituted benzoic acids, tending to prevent polymerization.
4. The position of the group and the temperature are probably factors in the polymerization of substituted benzoic acids. This is probably due to the variation in the solubility of the acids.
5. The method used is probably the best for carrying out this type of work.
6. Further work is being planned.

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B I O G R A P H Y

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