Reaction of Phenylvinylmethoxysulfonium Fluoroborate with Sodium Methoxide in Methanol.—To 3.1 g (12.2 mmoles) of phenylvinylmethoxysulfonium fluoroborate was added 1 equiv of sodium methoxide in methanol. The solvent was removed under vacuum and ether was added to the resultant slurry. After filtration and removal of the ether, an oil remained (2.0 g). The infrared spectrum was very similar to that of authentic phenyl 1,2-dimethoxyethyl sulfide. The mercuric chloride complex was prepared and recrystallized five times from a methanol–water mixture, mp 151–152°, melting point of authentic complex 151–152°, mixture melting point undepressed. The reaction was repeated employing deuteriomethanol. A mass spectrum of the distilled compound gave an M + 1 peak of 21.7% of the height of M, whereas product from the reaction with nondeuterated methanol gave an M + 1 peak of 12.6% (calcd 11.9%) indicating 8.3% deuterium incorporation in the former.

Phenyl 1,2-Dimethoxyethyl Sulfide.—To 4 ml of methanol at −70° were added 0.216 g (2 mmoles) of *t*-butyl hypochlorite, 0.272 g (2 mmoles) of phenyl vinyl sulfide, and 0.390 g (2 mmoles) of silver fluoroborate. The mixture was allowed to warm to room temperature and stirred for 3 hr after which ether was added. The ether solution was then extracted with sodium bicarbonate and dried with sodium sulfate. Removal of the solvent yielded 0.170 g of a liquid: bp 78–82° (0.1 mm); n^{27}_{D} 1.5404; nmr spectra aromatic complex at τ 2.75, quartet centered at 5.35 (proton α to oxygen and sulfur), two singlets at 6.54 and 6.76 (methoxy protons), and a multiplet between 6.5 and 6.7, partially obscured by the methoxy protons, representing the methylene group; infrared spectra (selected peaks) 2950, 1600, 1480, 1440, 1190, and a broad absorption at 1090–1130 cm^{-1}. A mass spectrum was taken and the molecular ion was found to be 198 (calcd 198). Other major peaks were at *m/e* 45, 51, 59, 65, 88, 89, 109, 110, 123, 135, 136, 153, and 168.

Reaction of *t*-Butylmethylmethoxysulfonium Fluoroborate with Sodium Ethoxide in Ethanol.—To 0.150 g (0.7 mmole) of *t*-butylmethylmethoxysulfonium fluoroborate was added 1 equiv of sodium ethoxide in dry ethanol. The acetaldehyde dimethone was prepared in 40% yield by the standard procedure, mp 138–139°, lit.[15] mp 140°. From a similar reaction the 2,4-dinitrophenylhydrazone was prepared in 58% yield, mp 147–149°, lit.[15] mp 147°. When mercuric chloride was added to the crude reaction mixture, a precipitate formed which was recrystallized twice from aqueous ethanol, mp 128–131°. The melting point of the authentic complex prepared from *t*-butyl methyl sulfide and mercuric chloride was found to melt at 128–131°. A mixture melting point with the complex was undepressed.

Registry No.—α-Methoxybenzyl sulfide, 5873-86-9; α-methoxyethyl phenyl sulfide, 10429-09-1; phenyl 1,2-dimethoxyethyl sulfide, 10429-08-0.

Quantitative Solubility–Structure Relationships for Some *meta*- and *para*-Substituted Benzoic Acids in *p*-Dioxane and in Tetrahydrofuran[1]

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The solubilities at 30° of benzoic acid and 14 *meta*- or *para*-substituted benzoic acids have been determined in *p*-dioxane and in tetrahydrofuran. The solubility values are reported in terms of grams of solute per 100 g of saturated solution, mole fraction of solute, and mole ratio of solute for each acid in each of the solvents. Analyses of the linear regression of log solubility ratio terms on Hammett's σ values are reported. Deviations are discussed and rationalized in terms of various factors which affect solubility. When the present data are compared with those reported previously for benzene and cyclohexane, correlations of the resulting log solubility ratio terms with Hammett's σ values produce V-shaped relationships.

In the first paper[2] of this series, values of log (X_B/X_C) at 30° for 20 *meta*- and *para*-substituted benzoic acids were reported. X_B and X_C are the mole fraction solubilities in benzene and in cyclohexane and, in general, are in the Henry's law range (X_B or X_C exceeded 0.05 in only two cases of the 40 values reported). For 16 of these acids, the correlation[3a] of log (X_B/X_C) with Hammett[4] σ values was highly significant at the 100.0% confidence level.[3b] Large deviations from this correlation were observed for the other four acids which are included among the five weakest of the 20 acids.

The purpose of the present study was to measure the solubilities of a similar series of benzoic acids in other solvents in which solute–solute interactions are minimized.

Coassociation of solute with solvent occurs[5] when intermolecular hydrogen bonds can be formed and association of the solute is thereby reduced. Consequently, *p*-dioxane and tetrahydrofuran were chosen as solvents because they are capable of dissociating dimeric carboxylic acids into single molecules by forming hydrogen bonds[6] and of minimizing solute–solute interactions which involve the substituent groups. If these solute–solute interactions can be minimized or cancelled, the solvent–solute interactions will predominate, and thus a good correlation of solubility with Hammett σ values may result.

Results and Discussion

The solubility in tetrahydrofuran and in *p*-dioxane at 30° of 15 benzoic acids, expressed as grams of acid per 100 g of saturated solution, as mole fraction solubility, and as mole ratio solubility, are given in Table I. From these data, values of log (X_T/X_D) and log (R_T/R_D) were calculated and are recorded in Table II. X_T and X_D are the mole fraction solubilities in tetrahydrofuran and in *p*-dioxane while R_T and R_D are the mole ratio solubilities in these two solvents. In contrast to the previously reported[2] X_B and X_C values, the values of X_T and X_D reported herein are, in general, much larger than 0.05 and are not in the Henry's law range. The solubilities of the benzoic acids were found to be greater in tetrahydrofuran than in *p*-dioxane.

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(1) Abstracted in part from the M.S. thesis of J. P. I., Texas A & M University, Jan 1965.

(2) C. K. Hancock, J. N. Pawloski, and J. P. Idoux, *J. Org. Chem.*, **31**, 3801 (1966).

(3) G. W. Snedecor, "Statistical Methods," 5th ed, The Iowa State College Press, Ames, Iowa, 1956: (a) Chapters VI, VII; (b) pp 46, 418, 441.

(4) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p 184.

(5) E. N. Lassettre, *Chem. Rev.*, **20**, 301 (1937).

(6) G. Allen and E. F. Caldin, *Quart. Rev.* (London), **7**, 278 (1953).

TABLE I

SOLUBILITIES OF SUBSTITUTED BENZOIC ACIDS IN TETRAHYDROFURAN AND IN *p*-DIOXANE AT 30°

No.[a]	Grams of acid/100 g of satd soln in Tetrahydrofuran	Grams of acid/100 g of satd soln in *p*-Dioxane	R_D[b]	R_T[c]	X_D[d]	X_T[e]
1	50.91	37.11	0.426	0.612	0.299	0.380
2	15.08	9.14	0.053	0.077	0.050	0.071
3	13.03	6.89	0.043	0.071	0.041	0.066
4	27.32	14.04	0.106	0.199	0.096	0.166
5	35.30	11.68	0.085	0.287	0.078	0.223
6	52.94	38.77	0.410	0.596	0.291	0.373
7	48.01	33.85	0.224	0.331	0.183	0.249
8	48.50	36.03	0.326	0.446	0.246	0.309
9	44.30	21.56	0.175	0.415	0.149	0.293
10	31.10	18.87	0.146	0.232	0.128	0.189
11	27.41	11.65	0.061	0.143	0.057	0.125
12	40.89	28.45	0.174	0.247	0.148	0.198
13	38.13	21.12	0.111	0.210	0.100	0.173
14	0.28	0.08	4.2×10^{-4}	1.2×10^{-3}	4.2×10^{-4}	1.2×10^{-3}
15	3.64	1.06	0.006	0.016	0.006	0.016

[a] Refers to acids as listed in Table II. [b] Mole ratio solubility in *p*-dioxane. [c] Mole ratio solubility in tetrahydrofuran. [d] Mole fraction solubility in *p*-dioxane. [e] Mole fraction solubility in tetrahydrofuran.

TABLE II

LOG RATIOS OF MOLE FRACTION SOLUBILITIES AND LOG RATIOS OF MOLE RATIO SOLUBILITIES OF SUBSTITUTED BENZOIC ACIDS ($RC_6H_4CO_2H$) IN *p*-DIOXANE AND IN TETRAHYDROFURAN AT 30°

No.	R	σ[a]	Log (X_T/X_D)	Log (R_T/R_D)
1	H	0.000	0.105	0.158
2	*p*-NO_2	0.778	0.150	0.160
3	*p*-OCH_3	−0.268	0.208	0.219
4	*p*-CH_3	−0.170	0.240	0.275
5	*p*-NH_2	−0.660	0.454	0.528
6	*m*-CH_3	−0.069	0.109	0.162
7	*m*-Br	0.391	0.133	0.169
8	*m*-OCH_3	0.115	0.010	0.136
9	*p*-OH	−0.357	0.294	0.374
10	*p*-F	0.062	0.170	0.191
11	3,4-Cl_2	0.600	0.337	0.370
12	4-Cl-3-NO_2	0.937	0.127	0.153
13	3,5-$(NO_2)_2$	1.420	0.238	0.275
14	*p*-CO_2H	0.265	0.468	0.469
15	*m*-CO_2H	0.355	0.456	0.461

[a] H. H. Jaffé, *Chem. Rev.*, **53**, 222 (1953).

TABLE III

CORRELATIONS BETWEEN SOLUBILITY IN TETRAHYDROFURAN AND IN *p*-DIOXANE AND HAMMETT σ VALUE AS THE INDEPENDENT VARIABLE

Entry	Dependent variable	Correlation coefficient, r	Std dev, s
1	Log (X_T/X_D)	−0.182	0.137
2	Log (R_T/R_D)	−0.262	0.134
3	Log X_T	−0.129	0.671
4	Log X_D	−0.080	0.772
5	Log R_T	−0.147	0.723
6	Log R_D	−0.087	0.810

From a statistical point of view alone, one might anticipate that this order would be reversed since, a *p*-dioxane molecule might associate with two acid molecules while a tetrahydrofuran molecule would associate with only one acid molecule. However, tetrahydrofuran is a more basic solvent than *p*-dioxane[7,8] and would therefore be expected to disrupt more readily the intermolecular hydrogen bonding in the benzoic acids and thus bring them into solution more easily.

The results of regression analyses[3a] of the data of Tables I and II are given in Table III. It is apparent from the r and s values in Table III that none of the six correlations is significant. Even so, in agreement with previous results,[2] the correlation between log (X_T/X_D) and σ is better than that between log X_T alone or log X_D alone and σ.

The very poor correlations found for entries 1 and 2 of Table III are most likely due to unfavorable non-Hammett solute–solute interactions resulting from the very high solubilities. The different interactions of the two solvents with the various acids, as described above, may be another cause for deviations from the Hammett relation since the solid phase in both solutions in each case is not in equilibrium with the same exact species in solution [*i.e.*, as pointed out previously[2,9] the relationship $\mu^*_2 - \mu^*_1 = RT \ln (X_1/X_2)$ holds only if the solute has the same mole fraction activity coefficient in the two solutions].[10] Also, in considering solubilities exhibited by a series of structurally related compounds RX (where R is varied while X remains constant), the solubility of RX is a function not only of a Hammett solubility effect due to variation in the solubility of the moiety X as caused by R but also of a non-Hammett intrinsic solubility effect due to compositional similarity of the R group, itself, with the solvent, these effects being manifested mainly in the form of the solvent–solute interactions. Consequently, the contribution of R to the solubility should be contained in the free-energy term to which the log ratio of solubilities is proportional.[2,9] However, the contribution of R to the solubility can arise from inductive, resonance, and other effects. Since the solubility measures the sum of all those interactions which can, in any manner, affect the solubility of the substituted benzoic acids, and since of the solvent–solute interactions which contribute to the free-energy term[2,9] only those due to

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[7] S. Searles and M. Tamnes, *J. Am. Chem. Soc.*, **73**, 3704 (1951).

[8] E. M. Arnett and C. Y. Wu, *ibid.*, **84**, 1684 (1962).

[9] M. Rapoport, C. K. Hancock, and E. A. Meyers, *J. Phys. Chem.*, **66**, 1752 (1962).

[10] Tetrahydropyran, which is approximately equal in basicity to tetrahydrofuran,[7,8,11] would probably have been a more desirable solvent than *p*-dioxane since its interaction with acid molecules would be similar to that for tetrahydrofuran.

[11] R. West, D. L. Powell, K. T. Lee, and L. S. Whatley, *J. Am. Chem. Soc.*, **86**, 3227 (1964).

specific chemical interaction of the functional group will be related to substituent constants, poor correlations occur here since all of the acids probably do not show the same type of interaction. Even though it would be very difficult to isolate any one particular chemical interaction, it seems reasonable that the physical effects of R itself and its electrical interaction with the ring could make such a large contribution to log (X_T/X_D) that chemical interaction involving the functional group would be overshadowed. For example, direct resonance interaction across the ring between certain of the R groups and the carboxylic acid group will result in a dipolar orientation causing interaction of the substituent group with the solvent and possible changes in solvation. If a change in solvation does occur, the nature of the solution process will not be the same for all of the compounds studied since direct resonance interaction of the type discussed above is not possible in some of the compounds under consideration. This effect of resonance and dipolar structures on solubility has been emphasized by Palit.[12] In the present case there is perhaps some indication of these differences in the solution process as shown in eq 1 and 2. Equation 1 applies to acids **1**,**3**–**6**, and **9**

$$\begin{array}{lcc} & r & s \\ \log (X_T/X_D) = 0.098 - \underset{(99.9)}{0.536\sigma} & -0.974 & 0.033 \end{array} \quad (1)$$

$$\begin{array}{lcc} \log (X_T/X_D) = 0.225 + \underset{(4.8)}{0.007\sigma} & 0.022 & 0.151 \end{array} \quad (2)$$

with electron-releasing substituents while eq 2 applies to acids **1**, **2**, **7**, **8**, and **10**–**15** with electron-withdrawing substituents. The numbers in parentheses below the coefficients of σ in eq 1 and 2 are the percentage confidence levels as determined by Student "*t*" tests.[3b] The fact that log (X_T/X_D) is a good measure of Hammett effects for one set of substituted benzoic acids with substituents having similar electrical effects but is a poor measure for another set having substituents of a different electrical nature emphasizes the importance of considering the resonance and possible solvation effects discussed above. This also indicates, as pointed out previously,[2] that there is not a localized "reaction" site, but rather the gross structure of the entire molecule plays an important role in the solution process.

The data reported in this article were combined with comparable data[2] for the solubilities of corresponding benzoic acids in benzene and in cyclohexane and are given in Table IV. For all 12 of the acids in Table IV, the correlation of any of the four log ratio solubility terms with σ is very poor, being comparable to entry 1 of Table III. In Table V, entries 7–10 applying only to acids **1**, **2**, **7**, **8**, and **11**–**13** with electron-withdrawing substituents show highly significant correlations, while in Table VI entries 11–14 applying only to acids **1**, **3**–**6**, and **9** with electron-releasing substituents show markedly improved correlations over those found for all 12 acids of Table IV.

TABLE IV

LOG RATIOS OF MOLE FRACTION SOLUBILITIES FOR SUBSTITUTED BENZOIC ACIDS IN TETRAHYDROFURAN, *p*-DIOXANE, CYCLOHEXANE, AND BENZENE AT 30°

No.[a]	Log (X_D/X_C)[b]	Log (X_D/X_B)[c]	Log (X_T/X_C)[b]	Log (X_T/X_B)[c]
1	1.320	0.555	1.424	0.660
2	3.629	2.483	3.779	2.632
3	2.807	1.393	3.015	1.600
4	1.584	1.017	1.824	1.257
5	3.831	2.264	4.286	2.718
6	1.211	0.438	1.320	0.547
7	2.060	1.255	2.193	1.388
8	1.698	0.745	1.797	0.844
9	3.605	3.404	3.899	3.698
11	2.997	1.893	3.334	2.231
12	3.831	2.339	3.958	2.466
13	4.157	2.343	4.395	2.581

[a] Refers to acids as listed in Table II. [b] X_C is the mole fraction solubility in cyclohexane and is from ref 2. [c] X_B is the mole fraction solubility in benzene and is from ref 2.

TABLE V

CORRELATIONS BETWEEN LOG RATIO SOLUBILITY TERMS AND σ FOR BENZOIC ACIDS WITH ELECTRON-WITHDRAWING SUBSTITUENTS (ACIDS **1**, **2**, **7**, **8**, and **11**–**13**)

Entry	Dependent variable	Intercept	Hammett ρ	r	s	Confidence level, %
7	Log (X_D/X_C)	1.49	2.19	0.958	0.352	99.9
8	Log (X_T/X_B)	0.89	1.54	0.896	0.411	99.4
9	Log (X_D/X_B)	0.77	1.46	0.895	0.394	99.3
10	Log (X_T/X_C)	1.61	2.27	0.958	0.365	99.9

TABLE VI

CORRELATIONS BETWEEN LOG RATIO SOLUBILITY TERMS AND σ FOR BENZOIC ACIDS WITH ELECTRON-RELEASING SUBSTITUENTS (ACIDS **1**, **3**–**6**, and **9**)

Entry	Dependent variable	Intercept	Hammett ρ	r	s	Confidence level, %
11	Log (X_D/X_C)	1.24	−4.53	−0.913	0.535	98.9
12	Log (X_T/X_B)	0.72	−4.02	−0.773	0.877	92.8
13	Log (X_D/X_B)	0.63	−3.49	−0.727	0.873	89.9
14	Log (X_T/X_C)	1.34	−5.06	−0.931	0.526	99.3

A plot of any of the four log ratios of mole fraction solubilities for all 12 acids given in Table IV *vs.* σ gives a V-shaped curve with a minimum near the point for unsubstituted benzoic acid, as illustrated in Figure 1 for log (X_D/X_C). In Figure 1, the line with negative slope is the line of entry 11 of Table VI for electron-releasing substituents, while the line with positive slope is the line of entry 7 of Table V for electron-withdrawing substituents. Thus, it appears that any of the four plots, as illustrated in Figure 1, for log (X_D/X_C) *vs.* σ, is not a random scatter of points but is, instead, a dual Hammett linear relationship with the two lines intersecting at a minimum near the point for unsubstituted benzoic acid.

In Figure 1 of the preceding article,[2] there was, perhaps, some indication of such a dual Hammett linear relationship for log (X_B/X_C) *vs.* σ. Inverted V-shaped Hammett plots have been reported[13] for the rates of the Wolff–Kishner reaction of hydrazones, and U-shaped Hammett plots have been reported[14] for the rates of solvolysis and of thiosulfate reactions of substituted α-chlorotoluenes. In both of these cases, the peculiar plots were rationalized in terms of different mechanisms for the two groups of compounds defined by the different lines. A similar analogy concerning the relationship represented by Figure 1 of the present article is tempting, but is difficult to make due to the complex-

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[12] S. R. Palit, *J. Phys. Chem.*, **51**, 837 (1947).

[13] H. H. Szmant and C. M. Harmuth, *J. Am. Chem. Soc.*, **86**, 2909 (1964).

[14] R. Fuchs and D. M. Carlton, *ibid.*, **85**, 104 (1963), and earlier references cited therein.

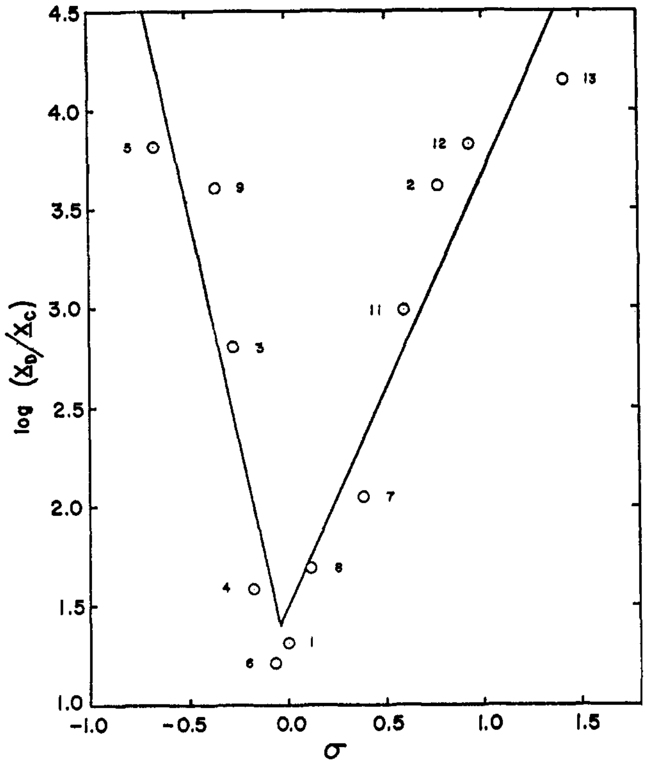

Figure 1.—Relationship between log (X_D/X_C) and σ for benzoic acids.

ity of the factors which affect the solution processes in the several solvents. In any event, the various log ratio of mole fraction solubility terms are fairly good indications of the Hammett effects involved in the solubilities.

Experimental Section

Materials—The *meta-* and *para-*substituted benzoic acids used in this study were procured and purified as reported previously.[2]

Practical grade *p*-dioxane and reagent grade tetrahydrofuran were left over sodium hydroxide pellets for 24 hr. In order to remove traces of water and peroxide,[15] the solvents were then passed through 2 × 70 cm chromatographic adsorption columns containing about 160 g of activated alumina. After this treatment, the nmr spectra indicated no impurities in the two solvents and their refractive indices agreed with previously reported values. The purified solvents were stored over copper in a nitrogen atmosphere. Quantities of the solvents purified at any one time did not exceed 2 l., and tests[16] indicated no peroxide content during use of the solvent (less than 2 weeks).

Solubility Determinations.—The saturated solutions were prepared and separated from excess solute as described previously,[2] except all flasks were purged with dry nitrogen before use. Solubilities in tetrahydrofuran were determined as described previously.[2]

The concentration of the saturated *p*-dioxane solutions was determined by titrating a weighed portion with standard sodium hydroxide solution (carbonate-free), using a Beckman Model Zeromatic pH meter equipped with a standard Beckman reference electrode and a Beckman glass electrode. The end point in each titration was determined by computing the second derivative of the change in pH with respect to the change in volume. The solubility of terephthalic acid in *p*-dioxane was determined by evaporation as described previously,[2] since good end points could not be obtained by titration.

The results of the above-mentioned methods were used to calculate the solubilities at 30° in terms of grams of solute/100 g of saturated solution, mole fraction of solute, and mole ratio of solute. These results are given in Table I.

Solubilities obtained by approaching equilibrium from undersaturation or from supersaturation agreed closely. For each of the acids, four determinations were made in each of the two solvents. In every case, two of the determinations were from the undersaturation side and two were from the supersaturation side. Based on mole fraction solubilities, the average deviation from the mean of replicate values was less than 1% for all of the acids except in the following cases: terephthalic acid in tetrahydrofuran and in *p*-dioxane, 5.9 and 3.9%; isophthalic acid in tetrahydrofuran and in *p*-dioxane, 1.1 and 2.4%. The maximum deviation from the mean of replicate values was less than 1% for all of the acids except in the following cases: terephthalic acid in tetrahydrofuran and in *p*-dioxane, 7.8 and 4.5%; isophthalic acid in tetrahydrofuran and in *p*-dioxane, 1.7 and 3.6%.

The tests for potential errors described in the preceding article[2] were carried out and indicated no appreciable errors from these sources.

To determine if the same results could be obtained by evaporation and by titration, saturated *p*-dioxane solutions of $C_6H_5CO_2H$, *p*-$CH_3OC_6H_4CO_2H$, and *p*-$O_2NC_6H_4CO_2H$ were evaporated and the solubilities were compared to those obtained by titration. The results of these tests showed good agreement for the first two acids. However, for *p*-nitrobenzoic acid, some of the acid was lost due to an unusually long period of time (about 30 hr) required for evaporation, and the resulting solubilities were low compared with the values obtained by titration.

Also, during the course of the study, the solubilities of several of the acids in tetrahydrofuran were determined by titration. In no case was there any significant difference between the solubilities obtained by the two methods.

Registry No.—**1,** 65-85-0; **2,** 62-23-7; **3,** 100-09-4; **4,** 99-94-5; **5,** 150-13-0; **6,** 99-04-7; **7,** 585-76-2; **8,** 586-38-9; **9,** 99-96-7; **10,** 456-22-4; **11,** 51-44-5; **12,** 96-99-1; **13,** 99-34-3; **14,** 100-21-0; **15,** 121-91-5; *p*-dioxane, 123-91-1; tetrahydrofuran, 109-99-9.

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(15) W. Dasler and C. D. Bauer, *Ind. Eng. Chem., Anal. Ed.*, **18**, 52 (1946).

(16) C. A. MacKenzie, "Experimental Organic Chemistry," 2nd ed, Prentice-Hall, Inc., Englewood Cliffs, N. J., 1962, p 108.