Summary

From determinations of the total solubility of the monochlorobenzoic acids in aqueous salt solutions the molecular solubilities and the activity coefficients have been obtained.

For the same weak acid some salts "salt-out" and others "salt-in." An explanation has been offered based on the work of Kruyt and Robinson.

The activity coefficients of the molecules of the monochlorobenzoic and benzoic acids are the same at corresponding concentrations of the same salt.

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The "Salting-out" and "Salting-in" of Weak Acids. II. The Activity Coefficients of the Molecules of Ortho, Meta and Para-Hydroxybenzoic Acids in Aqueous Salt Solutions[1]

BY ARTHUR OSOL AND MARTIN KILPATRICK

In the preceding paper it was shown that for the monochlorobenzoic acids the activity coefficients of the molecular part of these acids were the same at corresponding concentrations of the same salt. The present paper deals with the activity coefficients of ortho, meta and para-hydroxybenzoic acids.

Experimental Part

The experimental method was essentially the same as that given in the preceding paper. The acids were purified by recrystallization and melted at 159, 201 and 214° for the ortho, meta and para acids, respectively. The total solubilities were 0.01598, 0.0706 and 0.0451 mole per liter, from which the molecular solubilities at zero ion concentration, calculated from the K_a and K_c/K_a ratios as before, were found to be 0.01217, 0.0683 and 0.0440 mole per liter for the ortho, meta and para-hydroxy acids, respectively. The corrections for the buffer salts are given in each table. Table I gives the results in potassium chloride solutions.

From Table I it is evident that the activity coefficients are not the same for the three acids as in the case of the monochloro substituted acids. The "salting-out" constants decrease in the order ortho ($k = 0.122$), meta ($k = 0.115$), para ($k = 0.095$) as compared with benzoic acid ($k = 0.138$). Table II gives the results with sodium chloride.

The slope of the line for *o*-hydroxybenzoic acid in sodium chloride solutions in Fig. 1 is 0.172 as compared with 0.177 for benzoic acid.

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[1] Abstracted from the dissertation of Arthur Osol presented April 1, 1933, to the Faculty of the Graduate School of the University of Pennsylvania in partial fulfilment of the requirements for the degree of Doctor of Philosophy. Paper presented in part before the Washington meeting of the American Chemical Society, March, 1933.

TABLE I

SOLUBILITIES OF HYDROXYBENZOIC ACIDS IN POTASSIUM CHLORIDE SOLUTIONS

KCl moles per liter	Density, g. per cc.	Total acid, mole per liter	Mol. acid, mole per liter	"Salting-out" constant
o-Hydroxybenzoic Acid				
Solutions 0.01 molar in sodium salt. Correction = −0.00031				
0.2	1.008	0.01353	0.01144	0.132
.5	1.021	.01252	.01049	.129
1.0	1.042	.01096	.00919	.122
1.5	1.064	.00945	.00796	.123
2.0	1.087	.00833	.00704	.119
m-Hydroxybenzoic Acid				
Solutions 0.01 molar in sodium salt. Correction = −0.0002				
0.2	1.010	0.0657	0.0648	0.114
.5	1.024	.0606	.0596	.118
1.0	1.044	.0529	.0521	.118
1.5	1.067	.0470	.0463	.113
2.0	1.088	.0399	.0393	.119

KCl moles per liter	Density, g. per cc.	Total acid, mole per liter	Mol. acid, mole per liter	"Salting-out" constant
p-Hydroxybenzoic Acid				
Solutions 0.01 molar in sodium salt. Correction = −0.0002				
0.2	1.009	0.0430	0.0426	0.071
.5	1.023	.0399	.0395	.091
.7	1.030	.0381	.0377	.096
1.0	1.043	.0354	.0350	.099
1.5	1.066	.0323	.0320	.092
2.0	1.088	.0289	.0286	.094
2.5	1.109	.0256	.0253	.096

TABLE II

SOLUBILITIES OF *o*-HYDROXYBENZOIC ACID IN SODIUM CHLORIDE SOLUTIONS

NaCl moles per liter	Density, g. per cc.	Total acid, mole per liter	Mol. acid, mole per liter	"Salting-out" constant
Solutions 0.01 molar in sodium salt. Correction = −0.00031				
0.2	1.005	0.01326	0.01120	0.179
.5	1.018	.01188	.00993	.176
1.0	1.039	.00984	.00821	.171
2.0	1.076	.00666	.00556	.170

TABLE III

SOLUBILITIES OF *o*-HYDROXYBENZOIC ACID IN LITHIUM CHLORIDE SOLUTIONS

LiCl moles per liter	Density, g. per cc.	Total acid, mole per liter	Mol. acid, mole per liter	"Salting-out" constant
Solutions 0.01 molar in sodium salt. Correction = −0.00031				
0.5	1.010	0.01194	0.00979	0.189
.673	1.014	.01104	.00901	.194
1.198	1.025	.00882	.00713	.194
2.067	1.047	.00607	.00493	.190

TABLE IV

SOLUBILITIES OF *o*-HYDROXYBENZOIC ACID IN POTASSIUM BROMIDE SOLUTIONS

KBr moles per liter	Density, g. per cc.	Total acid, mole per liter	Mol. acid, mole per liter	"Salting-out" constant
Solutions 0.01 molar in sodium salt. Correction = −0.00031				
0.2	1.014	0.01381	0.01168	0.089
.5	1.038	.01308	.01099	.088
1.0	1.080	.01185	.00998	.086

TABLE V

SOLUBILITIES OF *o*-HYDROXYBENZOIC ACID IN SODIUM PERCHLORATE SOLUTIONS

$NaClO_4$ moles per liter	Density, g. per cc.	Total acid, mole per liter	Mol. acid, mole per liter	"Salting-out" constant
Solutions 0.01 molar in sodium salt. Correction = −0.00031				
0.472	1.034	0.01400	0.01190	0.021
.500	1.038	.01396	.01186	.022
1.000	1.076	.01338	.01155	.023
1.103	1.082	.01332	.01153	.021
1.863	1.141	.01215	.01075	.029

It is to be observed that for those salts producing the greatest decrease in solubility the differences in the values of *k* for benzoic and *o*-hydroxybenzoic acids are small. As shown in Table III the difference in the case of lithium chloride has disappeared. This is interpreted to mean that the effect of the introduction of the hydroxy group is to increase the "salting-in" by the anion, the effect being detectable for the larger cations which have smaller "salting-out" effects.

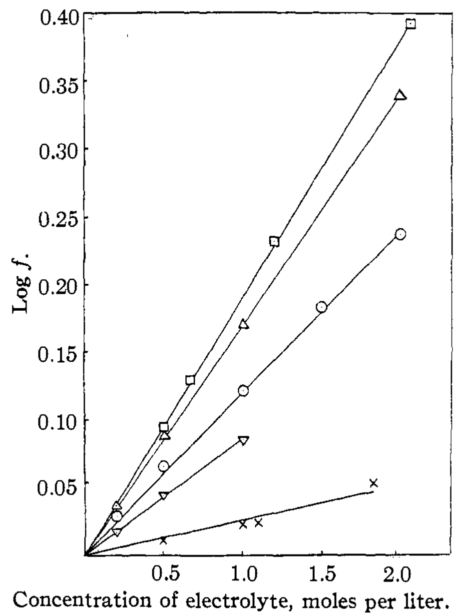

Fig. 1.—Activity coefficients of molecular *o*-hydroxybenzoic acid in salt solutions: ×, $NaClO_4$; ▽, KBr; △, NaCl; □, LiCl; ○, KCl.

In Tables IV and V the differences in the "salting-out" constants are still greater. Figure 1 presents graphically the results for salicylic acid. If our picture is correct, one would expect even greater "salting-in" constants (smaller activity coefficients) for the hydroxybenzoic acids in sulfonate solutions. Table VI shows this to be the case.

Table VII gives a comparison of the "salting-out" constants for the various salts which follow the law: $\log f = kC$.

TABLE VI

SOLUBILITIES OF *o*-HYDROXYBENZOIC ACID IN SULFONATE SOLUTIONS

Conc. sulfonate moles per liter	Density g. per cc.	Total acid, mole per liter	Mol. acid, mole per liter	"Salting-out" constant
Solutions 0.01 molar in sodium salt				
Correction = −0.00031				
In Sodium Benzenesulfonate				
0.10	1.005	0.01447	0.01234	−0.060
.25	1.015	.01545	.01307	− .124
.50	1.033	.01728	.01475	− .167
1.00	1.070	.02349	.02082	− .233
In Sodium *p*-Toluenesulfonate				
0.20	1.014	0.01677	0.01437	−0.361
.50	1.032	.02191	.01922	− .397
1.00	1.066	.03903	.03708	− .484
In Sodium β-Naphthalenesulfonate				
0.1	1.005	0.01790	0.01543	−1.03
.2	1.010	.02295	.01983	−1.06

The results for potassium chloride are given in Fig. 2. As shown in Fig. 3 of the preceding paper the results for the monochlorobenzoic acids coincide with those of benzoic acid. Evidently the introduction of the hydroxy group diminishes the decrease in solubility and increases the "salt-

TABLE VII

THE "SALTING-OUT" CONSTANTS FOR BENZOIC AND ORTHO-, META- AND PARA-HYDROXYBENZOIC ACIDS

Salt	Benzoic	o-Hydroxybenzoic	*m*-Hydroxybenzoic	*p*-Hydroxybenzoic
$NaClO_4$	0.060	0.026		
KBr	.108	.087		
KCl	.138	.122	0.115	0.095
NaCl	.177	.172		
LiCl	.192	.191		

ing-in" effect. The point of view that the molecules of the acid are more readily oriented on the anion upon the introduction of the polar hydroxy group seems to be in accord with the experimental results. In the case of other substituted benzoic acids it would appear that the effect of the introduction of a nitro group[2] would be similar to that of the chloride, while an amino group would have an effect like that of the hydroxy group.[3]

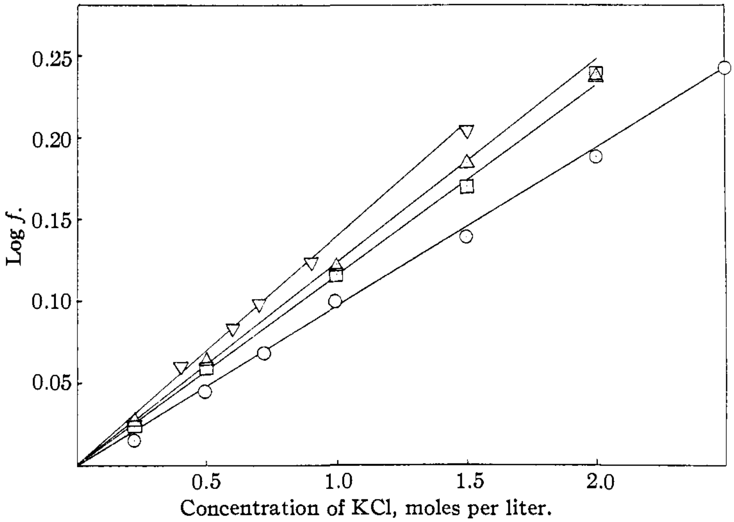

Fig. 2.—Activity coefficients of molecular benzoic, ortho, meta and para-hydroxybenzoic acids in KCl solutions: △, ortho; ○, para; □, meta; ▽, benzoic.

In concluding it should be pointed out that there should be cases in which the cation has a "salting-in" effect and the anion a "salting-out" effect, but in general the "salting-out" effect of the anions will probably be less than that of cations. One such case has been cited by Kruyt and Robinson from the data of Linderstrøm-Lang.[4]

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(2) Randall and Failey, *Chem. Rev.*, **4**, 291 (1927).

(3) Rørdam, Dissertation, Copenhagen, 1925.

(4) Kruyt and Robinson, *Proc. Acad. Amsterdam*, **29**, 1244 (1926); Linderstrøm-Lang, *Compt. rend. trav. lab. Carlsberg*, **15**, No. 4 (1924).

Summary

The activity coefficients of molecular salicylic acid have been determined in various aqueous salt solutions.

For the hydroxybenzoic acids the "salting-out" constants diverge from the values for benzoic acid as one progresses from salts having the highest "salting-out" effects to salts having the lowest effects.

A comparison of the "salting-out" constants for ortho, meta and para-hydroxybenzoic acids in potassium chloride solutions shows that the constants decrease with the transfer of the hydroxy group to the meta and para positions, respectively.

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Photochemical Studies. XVI. A Further Study of the Chlorination of Benzene

BY HOMER P. SMITH, W. ALBERT NOYES, JR., AND EDWIN J. HART

In a previous article[1] a report was made of an investigation of certain phases of the chlorination of benzene vapor. The results may be briefly summarized as follows. (1) The rate of reaction was at least approximately proportional to the pressure of the chlorine. Benzene and chlorine pressures of comparable magnitude (several centimeters) were used. (2) A liquid was formed first on the walls, followed by the gradual growth of crystals. The liquid was not analyzed. It may have been either phenyl chloride or a solution of benzene in some of the reaction products. (3) The only product isolated and for which a definite analysis was obtained was benzene hexachloride ($C_6H_6Cl_6$). (4) From measurements of pressure change and determination of the chlorine used up it was obvious that both addition and substitution were taking place.

In the present investigation an attempt has been made to elucidate certain aspects of benzene chlorination through measurements of quantum yields, pressure changes and reaction rates. In so far as the experimental results may be compared with those previously reported, complete agreement is noted. It was hoped to simplify the results by using benzene pressures so low that the first substitution product (phenyl chloride) would not condense.

I. Experimental Procedure

(a) **Chlorine.**—In some of the experiments the chlorine was prepared by heating anhydrous cupric chloride. Water was first removed from hydrated cupric chloride by heating for several days at 135° under a high vacuum. The chlorine was evolved at

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[1] Lane and Noyes, THIS JOURNAL, **54**, 161 (1932).