method which yields their determination of K seems to approach a much smaller limiting value than the simple mass action extrapolation in both cases.

In view of the failure of the theory to account for the conductance of sodium amide and the uncertainty of the treatment of potassium amide it would be useless to calculate ion sizes. If the underlying notions of the theory are at all justified it is certain, however, that the amide ion is exceedingly small. It may be that the unusual properties that have been found are specific for the amide ion but it seems more likely that they will prove rather to be characteristic of small ions in general.

V. Summary

The electrical conductance of sodium and potassium amide has been measured in liquid ammonia solution up to concentrations of 36,000 and 52,000 liters, respectively. The data for sodium amide deviate from the theory of Fuoss and Kraus as well as from the simple mass action theory. The agreement is better in the case of potassium amide but is not as good as might be desired. The results indicate that the specific properties of extremely small ions are important in the case of these electrolytes.

CAMBRIDGE, MASSACHUSETTS

RECEIVED JUNE 20, 1933
PUBLISHED NOVEMBER 7, 1933

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA]

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

BY ARTHUR OSOL AND MARTIN KILPATRICK

In general the solubility of a non-electrolyte is increased or decreased by the addition of an electrolyte, but the effect is not independent of the solvent salt. The results may be expressed by the equation

$$\log S_0/S = \log f \tag{1}$$

where S_0 is the solubility at zero ion concentration, S the solubility in the salt solution and f the activity coefficient of the non-electrolyte. It has been found that the equation

$$\log f = kC \tag{2}$$

C being the concentration of electrolyte in moles per liter and k a constant, holds over a wide range of concentration. The constant k is known as the "salting-out" constant. Provided a correction is made for the part

---

(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.

present as ions, equation (2) is applicable to weak electrolytes also. In most of the early work on acids this correction was neglected, or improperly made, with the result that (2) did not hold.[2] It has been mentioned that for a given non-electrolyte the effect depends upon the solvent salt. It is also true that in general, for a given solvent salt, the effect depends upon the saturating non-electrolyte.[3] The "salting-out" constant k generally increases with decrease in the polar properties of the non-electrolyte. This is the basis of the theory of Debye.[4]

The theory of Debye does not explain how certain salts "salt-out" a specified non-electrolyte while others salt it in. An explanation has been offered by Kruyt and Robinson.[5]

The point of view of Kruyt and Robinson is briefly as follows. In a solution of a non-electrolyte in water, the water dipoles are arranged about a molecule of non-electrolyte with their positive or negative end toward the non-electrolyte depending upon the polar properties of the latter. When an electrolyte is added to the solution, due to the hydration of the ions less water is available to the saturating non-electrolyte and on this basis alone "salting-out" of the non-electrolyte is expected. There is, however, a counteracting effect. Its polar nature determines whether the molecule of non-electrolyte attracts cations or anions. About the attracted ions water molecules are arranged in a manner opposite to the arrangement about the non-electrolyte and the result of the approach of the ion to the molecule of non-electrolyte is a packing in of water molecules about the molecules of non-electrolyte, *i. e.*, "salting-in." The effectiveness of the specified ion depends according to Kruyt and Robinson upon its degree of hydration. The non-electrolyte is "salted-out" if the first effect predominates and *vice versa.*

This paper concerns the solubility of molecular ortho, meta and para-chlorobenzoic acids in various salt solutions and compares the "salting-out" constants obtained with those found for benzoic acid.

Experimental Part

The experimental method was that of Chase and Kilpatrick.[2] In order to minimize the correction for the part present as ions, buffer solutions were used throughout the work.

The chlorobenzoic acids were purified by recrystallization from alcohol. They melted sharply at 139, 154 and 235° for the ortho, meta and para acids, respectively. The criterion of purity was constancy of solubility upon repeated treatment of the solid with water. Titrations were carried out in an atmosphere of nitrogen with carbonate

---

(2) Chase and Kilpatrick, THIS JOURNAL, **53**, 2589 (1931).

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

(4) Debye and McAulay, *Physik. Z.*, **26**, 22 (1925); Scatchard, THIS JOURNAL, **47**, 2069 (1925); *Chem. Rev.*, **3**, 383 (1927); Debye, *Z. physik. Chem.* (Cohen Festband), 56 (1927). For further references and a complete discussion see Falkenhagen, "Elektrolyte," S. Hirzel, Leipzig, 1933, p. 138–152.

(5) Kruyt and Robinson, *Proc. Acad. Amsterdam*, **29**, 1244 (1926). See also the very recent paper of P. M. Gross, *Chem. Rev.*, **13**, 91 (1933)

free sodium hydroxide. Weight burets were employed. When necessary the salts were purified by recrystallization.

The total solubility of *o*-chlorobenzoic acid in water was found to be 0.01362 mole per liter. Correction for the part present as ions was made by multiplying the K_c/K_a ratio[6] for benzoic acid given by Chase and Kilpatrick by K_a for *o*-chlorobenzoic acid (1.28×10^{-3}) and applying the mass law to the K_c thus found to obtain the hydrogen-ion concentration. The corresponding solubility of the molecular acid is 0.00986 mole per liter. In a similar manner the total solubilities of meta and para chlorobenzoic acids were found to be 0.00246 and 0.000435 and the corresponding molecular solubilities 0.00191 and 0.000275. Table I gives the solubilities of the acids in dilute solutions of sodium salts of the acids.

TABLE I

SOLUBILITIES OF CHLOROBENZOIC ACIDS IN SOLUTIONS OF THEIR SODIUM SALTS

o-Chlorobenzoic Acid

Sodium *o*-chlorobenzoate mole/liter	Density,[a] g. per cc.	Total acid mole per liter	H_3O^+, mole per liter	Molecular acid, mole per liter	$f = \frac{0.00990}{C_{o\mathrm{HClB}}}$
0.01	0.997	0.01131	0.00135	0.00996	0.994
.02	.999	.01085	.00080	.01005	.985
.05	1.002	.01059	.00035	.01024	.967
.0962	1.003	.01075	.00021	.01054	.939
.20	1.011	.01135	.00012	.01123	.882

m-Chlorobenzoic Acid

Sodium *m*-chlorobenzoate					$f = \frac{0.00191}{C_{m\mathrm{HClB}}}$
0.00212	0.997	0.00206	0.00014	0.00192	0.995

p-Chlorobenzoic Acid

Sodium *p*-chlorobenzoate					$f = \frac{0.000275}{C_{p\mathrm{HClB}}}$
0.000342	0.997	0.000343	0.000065	0.000278	0.989

[a] The densities are given so that other workers can express the results in molality if that is preferred.

These results will be discussed in connection with the experiments on "salting-in." They are put in at this point to give the magnitude of the corrections in the experiments with the other salts given in Tables II to XI. It might be mentioned that the value for the solubility of *o*-chlorobenzoic acid at zero ion concentration, 0.00990 was obtained by the method of least squares for all the "salting-out" experiments (see Figs. 1 and 2). For *m*- and *p*-chlorobenzoic acids the corresponding values are 0.00191 and 0.00275.

Table II gives the results with potassium chloride. The values in column four were obtained as before with correction for the "salting-in" of the sodium salt.

The slopes of the potassium chloride lines in Figs. 1, 2 and 3 are equivalent to values of $k = 0.139, 0.142, 0.138$, respectively. The corresponding value for benzoic acid is 0.138.[2]

---

(6) K_c represents the classical, K_a the thermodynamic, dissociation constant.

TABLE II

SOLUBILITIES OF CHLOROBENZOIC 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-Chlorobenzoic Acid Solutions 0.01 molar in sodium salt. Correction = −0.00007				
0.1	1.002	0.01137	0.00961	0.128
.3	1.012	.01086	.00905	.130
.5	1.021	.01014	.00843	.139
1.0	1.042	.00861	.00719	.139
2.0	1.087	.00607	.00515	.142
m-Chlorobenzoic Acid Solutions 0.00212 molar in sodium salt. Correction = −0.00001				
0.2	1.007	0.00199	0.00179	0.147
.5	1.020	.00183	.00163	.136
.75	1.031	.00167	.00149	.143
1.0	1.042	.00158	.00141	.133
1.5	1.064	.00127	.00114	.148
p-Chlorobenzoic Acid Solutions 0.000342 molar in sodium salt. Correction = −0.000003				
0.5	1.020	0.000331	0.000238	0.129
1.0	1.041	.000273	.000197	.146
1.5	1.063	.000235	.000172	.136
2.0	1.086	.000206	.000153	.128
2.5	1.107	.000156	.000118	.147

TABLE III

SOLUBILITIES OF CHLOROBENZOIC ACIDS 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
o-Chlorobenzoic Acid Solutions 0.01 molar in sodium salt. Correction = −0.00007				
0.2	1.005	0.01094	0.00915	0.171
.5	1.017	.00966	.00801	.182
2.0	1.076	.00498	.00422	.185
Solutions 0.02 molar in sodium salt. Correction = −0.00013				
0.5	1.018	0.00907	0.00806	0.179
1.0	1.039	.00739	.00658	.178
m-Chlorobenzoic Acid Solutions 0.00212 molar in sodium salt. Correction = −0.00001				
0.5	1.017	0.00174	0.00155	0.180
.75	1.027	.00156	.00140	.180
1.0	1.039	.00139	.00124	.187
2.0	1.076	.00094	.00085	.176

Table III gives the results with sodium chloride. Here and in all other cases the hydrogen-ion concentrations were calculated by combining the thermodynamic dissociation constant with the K_c/K_a ratios for each concentration of each salt as determined by Kilpatrick and Riesch by a catalytic method.[7] It seems reasonable to assume that the K_c/K_a ratios for the substituted benzoic acids are little different from the ratio for benzoic acid, in the given salt solution.[8]

Here and in Table IV it is shown that changing the buffer ratio makes no appreciable difference in the "salting-out" constant. In fact a comparison of the results for benzoic acid between buffered and unbuffered solutions showed that when proper corrections were applied the "salting-out" constants were the same in both cases. Studies in buffer solutions render the hydrogen-ion correction more certain.

The slopes of the lines for sodium chloride in Figs. 1 and 2 are 0.182 and

---

(7) Kilpatrick and Riesch, unpublished results.

(8) Larsson and Adell, *Z. physik. Chem.*, **157**, 342 (1931).

0.180. Berry[2] as well as Güntelberg and Schiödt[9] find 0.176 for benzoic acid at 20°, while Larsson[10] gives 0.177 at 18° and from the results of Kolthoff and Bosch[11] for benzoic acid at 25° values ranging from 0.181 to 0.199 are calculated.

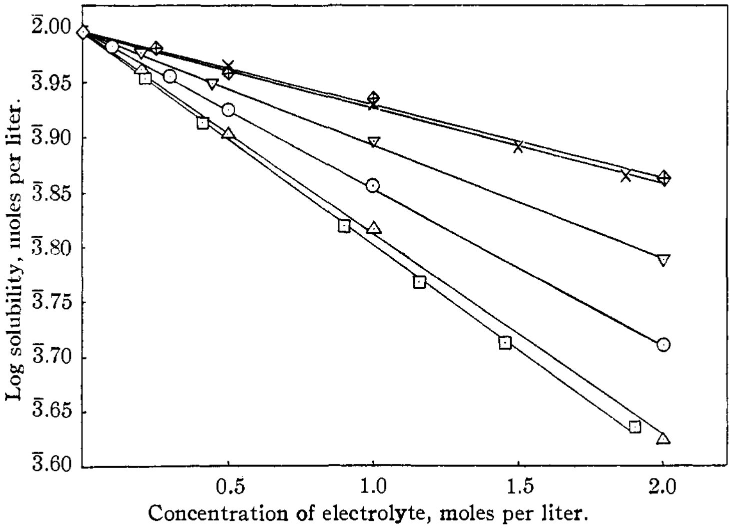

Fig. 1.—Solubilities of molecular *o*-chlorobenzoic acid in salt solutions: ×, $NaClO_4$; ▽, KBr; ○, KCl; △, NaCl; □, LiCl; ⊕, CsCl.

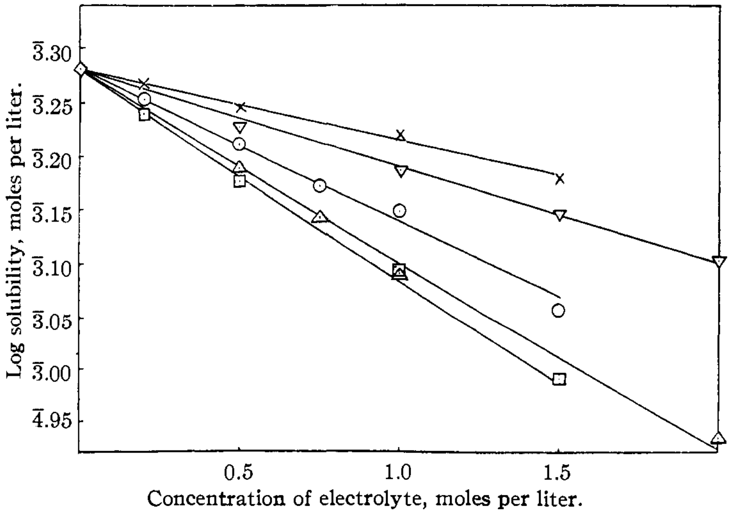

Fig. 2.—Solubilities of molecular *m*-chlorobenzoic acid in salt solutions: ×, $NaClO_4$; ○, KCl; △, NaCl; ▽, KBr; □, LiCl.

---

(9) Güntelberg and Schiödt, *Z. physik. Chem.*, **135**, 393 (1928).

(10) Larsson, *ibid.*, **153A**, 299 (1931).

(11) Kolthoff and Bosch, *J. Phys. Chem.*, **36**, 1685 (1932)..

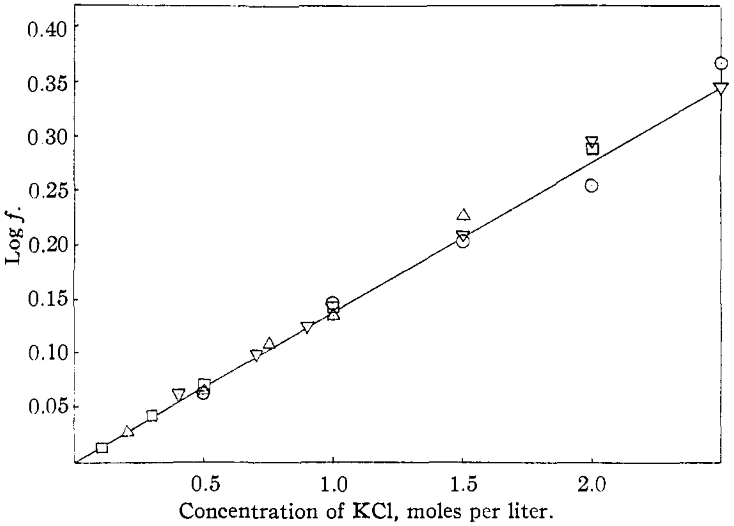

Fig. 3.—Activity coefficients of molecular benzoic, ortho, meta and para-chlorobenzoic acid in KCl solutions: ▽, benzoic; △, *m*-chlorobenzoic; □, *o*-chlorobenzoic; ○, *p*-chlorobenzoic.

TABLE IV

SOLUBILITIES OF CHLOROBENZOIC ACIDS 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
o-Chlorobenzoic Acid				
Solutions. 0.01 molar in sodium salt. Correction = −0.00007				
0.988	1.022	0.00797	0.00642	0.190
1.157	1.026	.00731	.00588	.195
1.458	1.032	.00645	.00518	.193
1.905	1.045	.00529	.00433	.189
Solutions 0.02 molar in sodium salt. Correction = −0.00013				
0.213	1.004	0.01018	0.00902	0.190
.415	1.007	.00939	.00822	.194
.901	1.020	.00763	.00665	.192
m-Chlorobenzoic Acid				
Solutions 0.00212 molar in sodium salt. Correction = −0.00001				
0.2	1.003	0.00196	0.00174	0.207
.5	1.009	.00172	.00151	.200
1.0	1.021	.00143	.00125	.185
1.5	1.034	.00112	.00098	.192

TABLE V

SOLUBILITIES OF CHLOROBENZOIC ACIDS 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
o-Chlorobenzoic Acid				
Solutions 0.01 molar in sodium salt. Correction = −0.00007				
0.2	1.017	0.01132	0.00949	0.091
.45	1.036	.01071	.00892	.100
1.0	1.083	.00943	.00789	.099
2.0	1.165	.00722	.00615	.103
m-Chlorobenzoic Acid				
Solutions 0.00212 molar in sodium salt Correction = −0.00001				
0.5	1.037	0.00190	0.00169	0.106
1.0	1.079	.00172	.00154	.093
1.5	1.121	.00156	.00140	.089
2.0	1.164	.00140	.00127	.089

The slopes of the lithium chloride lines in Figs. 1 and 2 are 0.193 and 0.193. Larsson finds for benzoic acid 0.192, while Kolthoff and Bosch give log *f* values from which constants may be obtained ranging from 0.186 to 0.213.

The slopes of the potassium bromide lines in Figs. 1 and 2 are 0.099 and 0.090. Larsson, reporting the solubilities of benzoic acid in three solutions, finds "salting-in" at the lowest concentration and gives the average value of *k* for the two others to be 0.070. Kolthoff and Bosch report activity coefficients which may be calculated to *k* values between 0.107 and 0.120. Haeseler's results are more complete and when corrected for the dissociated part give an average value of 0.113[12] at 25°.

TABLE VI

SOLUBILITIES OF CHLOROBENZOIC ACIDS 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
o-Chlorobenzoic Acid				
Solutions 0.01 molar in sodium salt. Correction = −0.00007				
0.25	1.016	0.01152	0.00962	0.050
.50	1.038	.01096	.00922	.061
1.00	1.076	.00995	.00852	.065
1.50	1.113	.00895	.00781	.068
1.87	1.142	.00834	.00737	.068
m-Chlorobenzoic Acid				
Solutions 0.00212 molar in sodium salt. Correction = −0.00001				
0.2	1.012	0.00206	0.00185	0.064
.5	1.037	.00197	.00176	.067
1.0	1.075	.00183	.00166	.061
1.5	1.112	.00166	.00151	.069

TABLE VII

SOLUBILITIES OF CHLOROBENZOIC AND BENZOIC ACIDS IN CESIUM CHLORIDE SOLUTIONS

CsCl moles per liter	Density, g. per cc.	Total acid, mole per liter	Mol. acid, mole per liter	"Salting-out" constant
o-Chlorobenzoic Acid				
Solutions 0.01 molar in sodium salt. Correction = −0.00007				
0.25	1.030	0.01134	0.00950	0.071
.50	1.062	.01094	.00910	.074
1.00	1.124	.01015	.00851	.066
2.00	1.245	.00854	.00730	.066
Benzoic Acid				
Solutions 0.01 molar in sodium salt. Correction = −0.0001				
0.2	1.024	0.0256	0.0252	0.108
.5	1.062	.0242	.0238	.093
1.0	1.124	.0223	.0220	.081

Here *k* for the sodium perchlorate lines is 0.065 in both Fig. 1 and Fig. 2. Larsson's value for benzoic acid at 18° is 0.050, while the results of Kolthoff and Bosch may be calculated to *k* values ranging from 0.051 to 0.080.

The slope of the cesium chloride line in Fig. 1 is 0.067. The two values given by Larsson for benzoic acid are "salting-in" constants indicating an increased solubility of molecular benzoic acid in solutions of cesium chloride. His calculations for *k* in 0.5 and 1.0 molar solutions are −0.008 and −0.009, respectively, at 18°. As this is the only case found in which there is a definite difference between the *k* values for *o*-chlorobenzoic acid and benzoic acid, solubility determinations were carried out with benzoic

---

(12) Haeseler, Dissertation, Columbia University, 1929.

acid in cesium chloride solutions at 25°. These values are given in the second part of Table VII.

The "salting-out" constant is 0.092, slightly higher than the values for *o*-chlorobenzoic acid and not in agreement with the values of Larsson for benzoic acid. The explanation is offered that while the activity coefficients seem to be independent of temperature for the case of marked decrease in solubility, this is not the case where the "salting-in" effect is playing a more important role.

In Figs. 1 and 2 it is seen that for the chlorides the order of decreasing solubility is as expected from the ion sizes, the greater effect being due to the smaller ion, *i. e.*, $Li > Na > K > Cs$. For the anions, however, in accordance with the theory one would expect that if the cations "salt-out" the anions would "salt-in" and although in this case the predominant effect is still "salting-out," a comparison of potassium bromide with potassium chloride and sodium perchlorate with sodium chloride shows this effect. We shall now turn to salts which definitely "salt-in" the chlorobenzoic acids.

"Salting-In" of Chlorobenzoic Acids.—The "salting-in" effect of sodium *o*-chlorobenzoate on *o*-chlorobenzoic acid has already been cited in Table I. A similar effect in the case of benzoic acid with sodium benzoate has been interpreted by Kolthoff and Bosch to be attributable to the formation of anions of double molecules of benzoic acid. The chief reason for not accepting compound formation as a general explanation is that potassium benzoate "salts-in" benzene and nitrobenzene, while potassium chloride "salts-out" these substances.[13] A definite case of a general "salting-in" effect which must be attributed to the polar structure of the non-electrolyte is the "salting-in" of trinitrotriamminecobalt by potassium chloride.[14]

Table VIII gives the results for *o*- and *m*-chlorobenzoic acids and benzoic acid in sodium benzenesulfonate solutions.

The results indicate that equation (2) no longer holds. The k values are not the same as those found by Larsson. For benzoic acid in 0.01 molar buffer solutions containing 0.2, 0.5 and 1.0 mole of sodium benzenesulfonate, Larsson obtains k values of -0.134, -0.117 and -0.120 (at 18°).

Table IX gives the results of solubility determinations of benzoic and *o*-chlorobenzoic acids in sodium *p*-toluenesulfonate solutions.

From Tables VIII and IX it is seen that the activity coefficient is apparently dependent on the buffer ratio. Table X gives the results with sodium β-naphthalenesulfonate as the solvent salt. Due to the slight solubility of this salt the results could not be extended above 0.2 molar.

---

(13) Private communication from P. M. Gross—from the Master's thesis of A. Whitenfish with J. H. Saylor and P. M. Gross.

(14) Brönsted, Delbanco and Volqvartz, *Z. physik. Chem.*, **162A**, 129 (1932).

Table VIII

Solubilities of Chlorobenzoic and Benzoic Acids in Sodium Benzenesulfonate Solutions

Sodium benzene-sulfonate moles/liter	Density, g. per cc.	Total acid, mole per liter	Mol. acid moles per liter	"Salting-out" constant
o-Chlorobenzoic Acid				
Solutions 0.01 molar in sodium salt. Correction = −0.00007				
0.2	1.011	0.01248	0.01045	−0.116
.5	1.032	.01381	.01164	− .140
.7	1.048	.01506	.01286	− .162
1.0	1.068	.01728	.01523	− .187
Solutions 0.05 molar in sodium salt. Correction = −0.00033				
0.5	1.033	0.01285	0.01199	−0.166
1.0	1.070	.01671	.01588	− .205
m-Chlorobenzoic Acid				
Solutions 0.00212 molar in sodium salt. Correction = −0.00001				
0.2	1.010	0.00226	0.00202	−0.122
.5	1.031	.00250	.00225	− .138
1.0	1.067	.00310	.00285	− .174
Benzoic Acid				
Solutions 0.01 molar in sodium salt. Correction = −0.0001				
0.1	1.005	0.0274	0.0270	−0.079
.2	1.011	.0280	.0276	− .089
.5	1.033	.0308	.0304	− .120
1.0	1.068	.0393	.0389	− .167
Solutions 0.05 molar in sodium salt. Correction = −0.0005				
0.2	1.013	0.0284	0.0278	−0.100
.5	1.034	.0313	.0307	− .128
1.0	1.071	.0417	.0411	− .190

Table IX

Solubilities of *o*-Chlorobenzoic and Benzoic Acids in Sodium *p*-Toluenesulfonate Solutions

Sodium *p*-toluene-sulfonate moles/liter	Density, g. per cc.	Total acid, mole per liter	Mol. acid, mole per liter	"Salting-out" constant
o-Chlorobenzoic Acid				
Solutions 0.01 molar in sodium salt. Correction = −0.00007				
0.2	1.011	0.01334	0.01130	−0.287
.5	1.032	.01668	.01447	− .329
.7	1.048	.01980	.01754	− .355
1.0	1.066	.02715	.02483	− .399
Solutions 0.05 molar in sodium salt. Correction = −0.00033				
0.2	1.015	0.01248	0.01166	−0.355
.3	1.022	.01364	.01276	− .367
.5	1.035	.01636	.01549	− .389
.7	1.048	.01964	.01877	− .397
1.0	1.069	.02721	.02630	− .425
Benzoic Acid				
Solutions 0.01 molar in sodium salt. Correction = −0.0001				
0.2	1.014	0.0305	0.0301	−0.278
.5	1.035	.0378	.0373	− .298
1.0	1.066	.0620	.0616	− .366

Discussion

A general survey of the results with any of the acids indicates that for the same weak acid some salts "salt-out" while others "salt-in." In general, it would appear that for the carboxylic acids investigated, the anion of the solvent salt has very little if any "salting-out" effect, but rather that its general effect is to increase the solubility. This is interpreted to mean that the molecules of weak acid are oriented about the anion.

A comparison of the activity coefficients of the chlorobenzoic acids

TABLE X

SOLUBILITIES OF *o*-CHLOROBENZOIC AND BENZOIC ACIDS IN SODIUM β-NAPHTHALENESULFONATE SOLUTIONS

Sodium β-naphthalene sulfonate moles/liter	Density, g. per cc.	Total acid, mole per liter	Mol. acid, mole per liter	"Salting-out" constant
o-Chlorobenzoic Acid				
Solutions 0.01 molar in sodium salt. Correction = −0.00007				
0.10	1.005	0.01382	0.01176	−0.747
.15	1.008	.01513	.01285	− .757
.20	1.010	.01693	.01432	− .802
Benzoic Acid				
Solutions 0.01 molar in sodium salt. Correction = −0.0001				
0.10	1.005	0.0313	0.0309	−0.670
.20	1.013	.0385	.0380	− .784

with benzoic acid is of particular interest in that the molecular solubility of the most soluble acid (benzoic) is approximately ninety-five times greater than the least soluble acid (*p*-chlorobenzoic) and the dissociation constant of the strongest acid (*o*-chlorobenzoic) is approximately twenty times greater than the weakest acid (benzoic). Table XI gives a summary of the "salting-out" constants for the different acids.

TABLE XI

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

Salt	Benzoic	*o*-Chlorobenzoic	*m*-Chlorobenzoic	*p*-Chloro benzoic
$NaClO_4$	0.060[a]	0.065	0.065	..
CsCl	.092[b]	.067	..	..
KBr	.108[c]	.099	.090	..
KCl	.138[d]	.139	.142	0.138
NaCl	.177[e]	.182	.180	..
LiCl	.192[f]	.193	.193	.

[a] Average value from Kolthoff and Bosch.

[b] Larsson gives −0.009 and −0.008 at 18°. See Table VII.

[c] Calculated from Haeseler's results (corrected).

[d] From the results of Chase and Kilpatrick.

[e,f] From Larsson.

From the table it is seen that in cases of "salting-out" the constant is practically the same for all four acids, that is, the activity coefficients of each acid are the same at the same concentration of a given salt. This is illustrated graphically for the case of potassium chloride as solvent salt in Fig. 3. Evidently this is a case in which a highly polar carboxyl group plays the predominating role in the "salting-in" process and the substitution of a chlorine atom in the phenyl group is without effect on the activity coefficient.

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.

PHILADELPHIA, PENNSYLVANIA RECEIVED JUNE 21, 1933
PUBLISHED NOVEMBER 7, 1933

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA]

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.

---

[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.