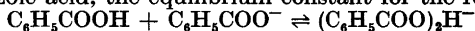


On the Existence of Acid Salts of Monocarboxylic Acids in Water Solutions

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The distribution coefficient of benzoic acid between water and toluene has been determined in the presence of sodium and potassium benzoate, sodium and potassium chloride and sodium bromide. The latter three salts had the same salting-out effect, whereas sodium and potassium benzoate had a salting-in effect. This difference is explained by complex formation between benzoic acid and benzoate ions. If all salts are considered to have the same salting-out effect on free benzoic acid, the equilibrium constant for the reaction



may be estimated to be 1.00 ± 0.03 in water at 25°.

In preparative organic chemistry the occurrence of acid salts of monocarboxylic acids of the composition $\text{RCOOH} \cdot \text{RCOOM}$, where M stands for an alkali metal, often gives rise to complications. When a strong acid is added to an alkaline solution of a carboxylic acid in water, a crystalline precipitate is often obtained which consists of the acid salt of the carboxylic acid. Sometimes the acid salt is very stable and even refluxing for 12 h with an excess of strong hydrochloric acid may not transform it to the corresponding acid. The acid salts are, however, usually readily soluble in alkaline solutions. If such a solution is slowly added to a rapidly stirred solution of an excess of a strong acid, the carboxylic acid is obtained without complications.

In spite of the fact that acid salts of, *e.g.*, acetic acid and benzoic acid are known as crystalline compounds and that it is well known that carboxylic acids are associated in the pure form or in organic solvents, the existence of acid salts of carboxylic acids in water solutions is usually overlooked. The main reason for this is probably that carboxylic acids seem to be present to only a minor extent as dimers in water.¹ It is also difficult to make accurate measurements of the acid salt concentration by ordinary methods. However, an accurate measurement of the distribution coefficient of benzoic acid between toluene and water will demonstrate the presence of the acid salt in the water solution.

In a toluene solution benzoic acid is present in the form of C_6H_5COOH and $(C_6H_5COOH)_2$ molecules. In a water solution it is present as C_6H_5COOH and $(C_6H_5COOH)_2$ molecules as well as $C_6H_5COO^-$ and $(C_6H_5COO)_2H^-$ ions. According to Nernst² the distribution law applies only to each individual form of the compound; if this is taken as C_6H_5COOH then the concentration term does not refer to the total concentration, but to this particular molecule.

The distribution coefficient for the C_6H_5COOH molecule between water and toluene can be determined by measuring the concentration of benzoic acid in both layers at several different concentrations of benzoic acid in the water layer. This is a standard procedure which is treated in some textbooks in physical chemistry.³ However, the possibility that complex formation may take place between the anion and the acid does not seem to have received any consideration.

CALCULATIONS

The following symbols are used in the calculations:

C^w	total concentration of acids in the aqueous layer
C^s	total » » » » organic layer
C_{HA}^w	concentration of C_6H_5COOH molecules in the aqueous layer
C_{HA}^s	» » » » » organic layer
$C_{H_2A_2}^w$	» » $(C_6H_5COOH)_2$ molecules in the aqueous layer
$C_{H_2A_2}^s$	» » » » » organic layer
$C_{A^-}^w$	» » $C_6H_5COO^-$ ions » » aqueous layer
$C_{HA_2^-}^w$	» » $C_6H_5COOH \cdot C_6H_5COO^-$ ions in the aqueous layer
F	distribution coefficient for C_6H_5COOH molecules
K_{ass}^s	association constant for C_6H_5COOH in the organic layer
K_a	protolytic constant of C_6H_5COOH in the aqueous layer
$k_{HA_2^-}$	dissociation constant of the complex $C_6H_5COOH \cdot C_6H_5COO^-$
γ	activity coefficient
μ	ionic strength
a	ionic radius in Ångström units
g	grams of benzoic acid
M	molecular weight of benzoic acid
σ	density of solid benzoic acid
V	volume of solvent

In the organic layer the following equations are valid:

$$C_{H_2A_2}^s = K_{ass}^s \cdot (C_{HA}^s)^2 \quad (I)$$

$$C^s = C_{HA}^s + 2C_{H_2A_2}^s \quad (II)$$

A combination of these gives

$$C^s = C_{HA}^s + 2K_{ass}^s (C_{HA}^s)^2 \quad (III)$$

For the distribution equilibrium of the C_6H_5COOH molecules we have

$$C_{HA}^s = FC_{HA}^w \quad (IV)$$

If IV is introduced into III the following equation is obtained

$$C^s/C_{HA}^w = F + 2K_{ass}^s F^2 C_{HA}^w \quad (V)$$

A plot of C^s/C_{HA}^w against C_{HA}^w should thus give a straight line with the slope $2K_{ass}^s F^2$ and the intercept F .

In eqn. V, C^s is accessible to direct measurements. However, this is not the case for C_{HA}^w , which must be calculated from C^w and some assumptions about $C_{H_2A_2}^w$ and $C_{HA_2^-}^w$. How this may be done is demonstrated below.

I. *Calculation of C_{HA}^w for a solution of benzoic acid in water containing neutral salts.* In a solution of benzoic acid in water containing neutral salts only, the following equations are valid

$$\frac{C_{A^-}^w C_{H_3O^+}}{C_{HA}^w} = \frac{K_a}{\gamma_{A^-} \gamma_{H_3O^+}} \quad (VI)$$

$$K_a = 6.14 \times 10^{-5} \text{ (Ref. 4)}$$

$$\log \gamma = \frac{0.511 \sqrt{\mu}}{1 + 0.329 a \sqrt{\mu}} \text{ (Ref. 4)} \quad (VII)$$

$$C^w = C_{HA}^w + 2C_{H_2A_2}^w + C_{HA_2^-}^w + C_{H_3O^+} \quad (VIII)$$

It has been demonstrated¹ that in the aqueous layer molecules of the type H_2A_2 are present only to a minute extent. For the anion HA_2^- we have the dissociation equilibrium $HA_2^- \rightleftharpoons HA + A^-$ and thus the equation

$$C_{A^-}^w C_{HA}^w = k_{HA_2^-} C_{HA_2^-}^w \quad (IX)$$

Preliminary experiments have demonstrated that $k_{HA_2^-}$ is about 1.0 and $C_{A^-}^w$ is small it follows that $C_{HA_2^-}^w$ is small compared with C_{HA}^w . Eqn. VIII thus becomes

$$C^w = C_{HA}^w + C_{H_3O^+} \quad (X)$$

Since the concentration of ions with negative charge must be the same as the concentration of ions with positive charge it follows that

$$C_{A^-}^w = C_{H_3O^+} \text{ (} C_{OH^-} \text{ is very small)} \quad (XI)$$

From the experimental values of K_a and a (Ref. 4) and the eqns. VI, VII, X, and XI, C_{HA}^w is readily calculated for each value of C^w .

All measurements of C^w were carried out by titrations in dilute solutions ($C^w < 15$ mM). The presence of carbon dioxide will thus give rise to a small error since it is titrated together with the benzoic acid. Blank determinations demonstrated that the concentration of carbon dioxide was 0.028 mM which was therefore subtracted from the C^w values obtained in the titrations.

In most cases C^w was also checked by measuring the light absorption of a sample in 0.01 M hydrochloric acid. The results obtained by these two methods were identical to within 0.5 %. Those obtained by the titration method had a reproducibility of better than 0.2 %. C^s was calculated with the help of the equation

$$C^s = \frac{g}{M(V + g/\sigma)} \quad (XII)$$

where g/M is the difference between the number of moles of benzoic acid weighed out and that found in the water layer. The term g/σ is introduced to correct for the small volume change in the organic layer caused by the benzoic acid.

The results are given in Tables 1–5. It is readily seen that they fit an equation of the type V. In Table 6 the values of C_{HA}^w obtained by interpolations in Tables 1–5 are given for 5 fixed values of C^s . From this it is obvious that the non protolytic salts have a salting out effect on the C_6H_5COOH molecules

Table 1. Distribution of benzoic acid between water and toluene. Correction used for $C^w = -0.028$ mM. Concentration in mM.
 $C^s/C_{HA}^w = 1.09 + 1.009C_{HA}^w$.

C^w	C_{HA}^w	C^s	C^s/C_{HA}^w	
			found	calc.
0.920	0.707	1.257	1.78	1.80
1.487	1.209	2.784	2.30	2.31
2.317	1.962	5.940	3.03	3.07
3.560	3.115	12.98	4.17	4.23
5.216	4.668	27.47	5.89	5.80
7.660	6.987	57.34	8.21	8.14
11.09	10.27	118.1	11.50	11.45
15.86	14.87	239.1	16.08	16.09

Table 2. Distribution of benzoic acid between 0.1 M NaCl and toluene. Correction used for $C^w = -0.028$ mM. Concentration in mM.
 $C^s/C_{HA}^w = 1.28 + 1.106C_{HA}^w$.

C^w	C_{HA}^w	C^s	C^s/C_{HA}^w	
			found	calc.
3.435	2.91	13.11	4.51	4.50
5.11	4.46	27.85	6.24	6.21
7.44	6.65	57.05	8.58	8.63
10.73	9.78	118.6	12.12	12.10
15.30	14.15	239.6	16.93	16.93

Table 3. Distribution of benzoic acid between 0.2 M NaCl and toluene. Correction used for $C^w = -0.028$ mM. Concentration in mM.
 $C^s/C_{HA}^w = 1.12 + 1.228C_{HA}^w$.

C^w	C_{HA}^w	C^s	C^s/C_{HA}^w	
			found	calc.
3.38	2.84	13.01	4.58	4.61
5.00	4.34	27.83	6.41	6.45
7.20	6.38	57.57	9.02	8.95
10.37	9.38	119.3	12.71	12.64
14.74	13.56	240.2	17.72	17.77

which is the same for the different neutral salts and which increases with increasing ionic strength.

II. *The distribution equilibrium in the presence of alkali benzoates.* If benzoic acid is dissolved in an aqueous solution of an alkali benzoate, it is readily seen from eqn. VI that $C_{H_3O^+}$ is very low compared with C_{HA}^w .

Table 4. Distribution of benzoic acid between 0.1 M NaBr and toluene. Correction used for $C^w = -0.03$ mM. Concentration in mM.

$$C^s/C_{HA}^w = 1.32 + 1.098C_{HA}^w.$$

C^w	C_{HA}^w	C^s	C^s/C_{HA}^w	
			found	calc.
3.44	2.91	13.11	4.51	4.52
5.12	4.47	27.76	6.21	6.23
7.44	6.65	57.32	8.62	8.62
10.73	9.78	118.7	12.14	12.08
15.35	14.20	239.5	16.87	16.91

Table 5. Distribution of benzoic acid between 0.1 M KCl and toluene. Correction used for $C^w = -0.03$ mM. Concentration in mM.

$$C^s/C_{HA}^w = 1.35 + 1.094C_{HA}^w.$$

C^w	C_{HA}^w	C^s	C^s/C_{HA}^w	
			found	calc.
3.43	2.90	13.06	4.50	4.52
5.10	4.45	27.68	6.22	6.22
7.41	6.62	57.08	8.62	8.59
10.76	9.81	118.64	12.09	12.08
15.34	14.19	239.29	16.86	16.89

Table 6. Concentrations of HA and HA + H₂A⁻ in different solutions in contact with toluene solutions of fixed concentrations.

Solution	Acid	Concentrations, mM				
		13.00	28.00	57.00	119.0	240.0
toluene	HA + H ₂ A ₂					
water	HA	3.12	4.72	6.97	10.31	14.90
0.1 M NaCl	HA	2.90	4.47	6.65	9.80	14.16
0.1 M NaBr	HA	2.90	4.49	6.63	9.79	14.22
0.1 M KCl	HA	2.89	4.48	6.61	9.83	14.21
0.2 M NaCl	HA	2.84	4.36	6.35	9.37	13.56
0.1 M NaA	HA + H ₂ A ⁻	3.23	5.01	7.45	10.93	15.71
0.1 M KA	HA + H ₂ A ⁻	3.15	4.85	7.19	10.74	15.51
0.2 M NaA	HA + H ₂ A ⁻	3.41	5.18	7.69	11.19	16.26
0.1 M NaCl + 0.1 M NaA	HA + H ₂ A ⁻	3.01	4.65	6.93	10.17	14.73

Since $C_{H_2A_1}^w$ is also very low eqn. VIII gives

$$C^w = C_{HA}^w + C_{HA_1}^w \quad (\text{XIII})$$

C^w is readily determined by titration with standard alkali to a pH which corresponds to eqn. VI and the end point condition $C_{HA}^w = C_{OH^-}$.

An error in the calculation and determination of the endpoint by ± 0.5 pH unit will introduce an error of about 0.5 to 1.0 % in C^w . Since the pH of the endpoint is readily calculated and determined with an error of less than ± 0.1 pH unit the titration is easily performed to give titration errors less than 0.2 %.

The alkali benzoate solutions were prepared from benzoic acid and alkali hydroxides with low CO_2 content and adjusted to exactly the correct pH value. The CO_2 content gives rise to a small error. On the addition of benzoic acid CO_2 is liberated, which is partly dissolved in the organic layer. This results in a decrease in the total quantity of benzoic acid not present as an alkali benzoate and thus to an error in C^s . It also gives a too high value of C^w in the titration. Both these factors can be determined by blank determinations and thus corrected for. The corrections are very small and do by no means obscure the results.

If $C_{\text{HA}_2}^{-w}$ is small compared with C_{HA}^w eqn. XIII is simplified to $C^w = C_{\text{HA}}^w$. In Table 6 the values for $C^w = C_{\text{HA}}^w + C_{\text{HA}_2}^{-w}$ are given for the 5 fixed values of C^s . It is readily seen that the values of C^w obtained in the presence of benzoate ions are much higher than those of C_{HA}^w obtained in the presence of the non protolytic salts, and are even higher than the values of C_{HA}^w obtained without any salt present. The benzoate ion should thus have a salting-in effect in contrast to the salting-out effect of the halide ions. Such a difference is hard to explain in any other way than by complex formation between the benzoate ion and benzoic acid which means that the concentration of the complex $C_{\text{HA}_2}^{-w}$ cannot be insignificant.

If eqn. XIII is combined with eqn. IX the result is

$$C_{\text{HA}}^w = \frac{C^w k_{\text{HA}_2}^-}{C_{\text{A}^-}^w + k_{\text{HA}_2}^-} \quad (\text{XIV})$$

C_{HA}^w cannot be directly calculated by this equation since $k_{\text{HA}_2}^-$ is not known. Introducing XIV into V gives

$$\frac{C^s}{C^w} = F \frac{k_{\text{HA}_2}^-}{C_{\text{A}^-}^w + k_{\text{HA}_2}^-} + 2F^2 K_{\text{ass}}^s \left(\frac{k_{\text{HA}_2}^-}{C_{\text{A}^-}^w + k_{\text{HA}_2}^-} \right)^2 C^w \quad (\text{XV})$$

A plot of C^s/C^w against C^w should thus give a straight line with the slope

$$2F^2 K_{\text{ass}}^s \left(\frac{k_{\text{HA}_2}^-}{C_{\text{A}^-}^w + k_{\text{HA}_2}^-} \right)^2$$

Table 7. Distribution of benzoic acid between 0.1 M sodium benzoate and toluene. Correction used for $C^w = -0.03$ mM, and for $C^s = -0.46$ mM. Concentrations in mM. $C^s/C^w = 1.05 + 0.901 C^w$.

C^w	C^s	C^s/C^w	
		found	calc.
3.18	12.69	3.99	3.92
4.93	27.16	5.51	5.49
7.46	57.15	7.66	7.77
10.88	117.9	10.83	10.85
15.68	239.0	15.24	15.18

Table 8. Distribution of benzoic acid between 0.2 M sodium benzoate and toluene. Corrections used for $C^w = -0.03$ mM and for $C^s = -0.50$ mM. Concentrations in mM. $C^s/C^w = 0.93 + 0.854 C^w$.

C^w	C^s	C^s/C^w .	
		found	calc.
3.34	12.56	3.76	3.78
5.10	27.20	5.33	5.29
7.69	56.97	7.41	7.50
11.12	117.7	10.59	10.43
16.19	238.1	14.70	14.76

Table 9. Distribution of benzoic acid between 0.1 M potassium benzoate and toluene. Corrections used for $C^w = -0.03$ mM and for $C^s = -0.26$ mM. Concentrations in mM. $C^s/C^w = 1.31 + 0.913 C^w$.

C^w	C^s	C^s/C^w	
		found	calc.
2.99	11.91	3.98	4.04
4.71	26.62	5.65	5.61
7.12	56.05	7.87	7.81
10.66	117.24	11.00	11.04
15.45	238.3	15.42	15.41

Table 10. Distribution of benzoic acid between toluene and an aqueous solution 0.1 M in sodium chloride and 0.1 M in sodium benzoate. Corrections used for $C^w = -0.03$ mM and for $C^s = -0.50$ mM. $C^s/C^w = 1.24 + 1.022 C^w$.

C^w	C^s	C^s/C^w	
		found	calc.
3.06	13.38	4.37	4.37
4.68	28.27	6.04	6.02
6.97	57.94	8.31	8.36
10.18	119.15	11.70	11.64
14.74	240.16	16.29	16.30

The values obtained are given in Tables 7–10. It is readily seen that they fit an equation of the type given in eqn. XV.

In these plots C_A^{-w} has been considered as a constant equal to the original concentration of the benzoate. This is not absolutely correct since the formation of HA_2^- decreases the actual concentration of A^- . Since preliminary experiments have shown that $C_{HA_2^-}^{-w}$ is small compared with C_A^{-w} and $k_{HA_2^-}$ the error introduced is without practical importance. The straight lines obtained in the plots of C^s/C^w against C^w will be used to calculate C^w values at fixed C^s values.

Calculation of $k_{\text{HA}_2^-}$. It has now been found that sodium chloride, sodium bromide, and potassium chloride of the same ionic strength have the same salting-out effect on benzoic acid. If it is assumed that solutions of uni-univalent electrolytes of the same ionic strengths have the same salting-out effect and that the difference is due to complex formation, $k_{\text{HA}_2^-}$ can be calculated in the following way.

Table 11. Formation of HA_2^- in a 0.1 M sodium benzoate solution. Concentration in mM. $k_{\text{HA}_2^-} = 0.94$.

C^s	13.00	28.00	57.00	119.0	240.0
$C_{\text{HA}^w} + C_{\text{HA}_2^-w}$	3.23	5.01	7.45	10.93	15.71
C_{HA^w}	2.90	4.48	6.63	9.81	14.21
C_{A^-w}	99.7	99.5	99.2	98.9	98.5
$C_{\text{HA}^w}C_{\text{A}^-w}$	289	446	658	970	1399
$C_{\text{HA}_2^-w}$ found	0.33	0.53	0.82	1.12	1.51
$C_{\text{HA}_2^-w}$ calc.	0.37	0.54	0.76	1.09	1.55

Table 12. Formation of HA_2^- in a 0.2 M sodium benzoate solution. Concentrations in mM. $k_{\text{HA}_2^-} = 0.99$.

C^s	13.00	28.00	57.00	119.0	240.0
$C_{\text{HA}^w} + C_{\text{HA}_2^-w}$	3.41	5.18	7.69	11.19	16.26
C_{HA^w}	2.84	4.36	6.35	9.37	13.56
C_{A^-w}	199.4	199.2	198.7	198.2	197.3
$C_{\text{HA}^w}C_{\text{A}^-w}$	566	866	1259	1859	2675
$C_{\text{HA}_2^-w}$ found	0.57	0.82	1.34	1.82	2.70
$C_{\text{HA}_2^-w}$ calc.	0.55	0.87	1.26	1.87	2.70

Table 13. Formation of HA_2^- in an aqueous solution 0.1 M in NaCl and 0.1 M in sodium benzoate. Concentration in mM. $k_{\text{HA}_2^-} = 1.04$.

C^s	13.00	28.00	57.00	119.0	240.0
$C_{\text{HA}^w} + C_{\text{HA}_2^-w}$	3.01	4.65	6.93	10.17	14.73
C_{HA^w}	2.84	4.36	6.35	9.37	13.56
C_{A^-w}	99.9	99.7	99.5	99.2	98.8
$C_{\text{HA}^w}C_{\text{A}^-w}$	284	434	632	930	1340
$C_{\text{HA}_2^-w}$ found	0.17	0.29	0.58	0.80	1.17
$C_{\text{HA}_2^-w}$ calc.	0.17	0.32	0.51	0.79	1.19

Table 14. Formation of HA_2^- in a 0.1 M potassium benzoate solution. Concentration in mM. $k_{\text{HA}_2^-} = 1.02$.

C^s	13.00	28.00	57.00	119.0	240.0
$C_{\text{HA}^w} + C_{\text{HA}_2^-w}$	3.15	4.85	7.19	10.74	15.51
C_{HA^w}	2.90	4.48	6.63	9.81	14.20
C_{A^-w}	998	996	994	990	986
$C_{\text{HA}^w}C_{\text{A}^-w}$	289	446	658	971	1400
$C_{\text{HA}_2^-w}$ found	0.25	0.37	0.56	0.93	1.31
$C_{\text{HA}_2^-w}$ calc.	0.22	0.38	0.59	0.89	1.32

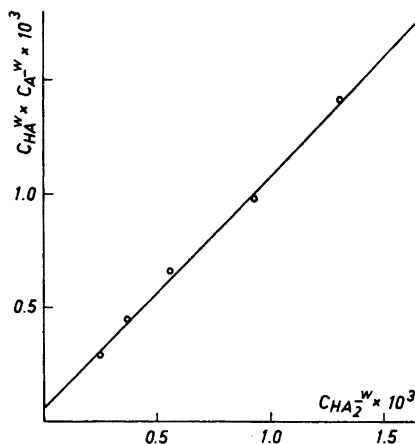


Fig. 1. Formation of HA_2^- in a 0.1 M potassium benzoate solution.

Solutions of the same ionic strength in contact with toluene solutions of identical C^s values should have the same C_{HA}^w values. In Tables 6 the values of C_{HA}^w and $C_{\text{HA}}^w + C_{\text{HA}_2^-}^w$ obtained by interpolation in Tables 1–10 are given for some fixed values of C^s . From these values $C_{\text{HA}_2^-}^w$ is readily calculated. All the values C_{HA}^w , $C_{\text{A}^-}^w$ and $C_{\text{H}_2\text{A}}^w$ necessary to calculate $k_{\text{HA}_2^-}$ by means of eqn. IX are thus accessible. The calculation of $k_{\text{HA}_2^-}$ is probably best performed by plotting $C_{\text{A}^-}^w \cdot C_{\text{HA}}^w$ against $C_{\text{HA}_2^-}^w$. In this way a straight line is obtained with the slope $k_{\text{HA}_2^-}$. The results are given in Tables 11–14. The calculated values are those obtained from the best plot. It can be seen that the agreement between the found and calculated values is good and that $k_{\text{HA}_2^-}$ is reasonably constant, and equal to 1.00 ± 0.03 .

The fact that the best plots (Fig. 1) do not go exactly through the origin is probably due to the use of an incorrect blank in correcting the C^w values for the CO_2 content. This gives rise to a constant error in $C_{\text{HA}_2^-}^w$ and will not effect the slope $k_{\text{HA}_2^-}$ of the plot.

The accuracy obtainable in the determination of a distribution coefficient is thus high enough to permit the determination of the equilibrium constant for the association of the acid with the anion. This association seems to be appreciable for benzoic acid and should not be overlooked in exact calculations.

EXPERIMENTAL

The distributions were determined by a standard procedure¹ with the modification that an automatic titrator (Titrator type TTT 1 with Titrigraph type SBR2/SBUI from Radiometer) was used for the titrations. The author is indebted to Mr. Karel Kavale for the experimental work presented here.

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