

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

THE CLASSICAL DISSOCIATION CONSTANT OF BENZOIC ACID AND THE ACTIVITY COEFFICIENT OF MOLECULAR BENZOIC ACID IN POTASSIUM CHLORIDE SOLUTIONS^{1,2}

BY ELWYN F. CHASE AND MARTIN KILPATRICK, JR.

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In a previous paper³ the authors reported the hydrogen-ion concentration of a series of benzoic acid-benzoate buffers in aqueous potassium chloride solutions. From these values and the composition of the buffer the product of the concentration of hydrogen and benzoate ions was calculated. In all cases the solutions were saturated with benzoic acid so that a determination of the solubility of the acid in these solutions enables one to calculate the classical dissociation constant and the activity coefficient of the molecular benzoic acid. The solubility of the molecular acid is obtained by subtracting the hydrogen-ion concentration from the total concentration of benzoic acid as determined by titration. Column 3 of Table I gives the solubility of benzoic acid in the various solutions and Column 5 gives the amount present as molecular acid.

TABLE I
THE SOLUBILITY OF BENZOIC ACID IN POTASSIUM CHLORIDE SOLUTIONS AT 25.15°

Electrolyte KCl + NaB	Moles per liter			Molecular benzoic acid	Average
	Benzoate × 10 ⁶	Total benzoic acid	C _{H+} × 10 ⁶		
0.0013	131.0	0.02781	131.0	0.02650	0.02650
.1000	529.4	.0261	48.5	.0256	
	767.3	.0256	32.8	.0253	
	1025	.0259	25.1	.0256	.0255
.2000	761.6	.0251	34.3	.0248	
	1660	.0250	15.9	.0248	
	3301	.0254	7.79	.0253	.0250
.3000	1663	.0242	15.6	.0240	
	1744	.0241	15.0	.0239	
	2481	.0244	10.5	.0243	
	3301	.0244	7.94	.0243	.0241
.4000	1663	.0235	15.6	.0233	
	1744	.0228	15.0	.0226	
	2480	.0229	10.2	.0228	
	3302	.0236	7.82	.0235	.0231

¹ Abstracted from the thesis of Elwyn F. Chase presented to the Faculty of the Graduate School of the University of Pennsylvania in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

² Paper presented before the Indianapolis meeting of the American Chemical Society, March 30–April 3, 1931.

³ Kilpatrick and Chase, *THIS JOURNAL*, **53**, 1732 (1931).

TABLE I (Concluded)

Electrolyte KCl + NaB	Moles per liter				Average
	Benzoate $\times 10^5$	Total benzoic acid	$C_{H^+} \times 10^3$	Molecular benzoic acid	
0.5000	320.5	0.0232	80.1	0.0224	0.0225
	1989	.0223	12.9	.0222	
	4329	.0231	5.78	.0230	
.6000	1662	.0220	15.0	.0218	.0219
	1743	.0219	14.3	.0218	
	2480	.0221	10.0	.0220	
.7000	1661	.0213	14.3	.0212	.0213
	2480	.0213	9.64	.0212	
	3300	.0216	7.09	.0215	
.9000	1661	.0199	13.5	.0198	.0199
	2479	.0200	8.88	.0199	
	3300	.0202	6.60	.0201	
1.012	874.3	.0184	24.3	.0182	.0190
	1334	.0192	15.8	.0190	
	1660	.0193	12.8	.0192	
	1987	.0191	10.5	.0190	
	3299	.0191	5.97	.0190	
	3336	.0193	6.36	.0192	
	4328	.0190	4.66	.0190	
	5004	.0194	4.14	.0194	
1.500	296.2	.0169	55.8	.0163	.0166
	1861	.0168	8.98	.0167	
	1984	.0164	8.17	.0163	
	4329	.0170	3.67	.0170	
2.000	635.8	.0135	18.3	.0133	.0137
	1245	.0138	10.1	.0137	
	1859	.0141	6.53	.0140	
	4301	.0139	2.81	.0139	
2.500	632.3	.0120	14.8	.0119	.0121
	1242	.0121	7.42	.0120	
	1980	.0123	4.54	.0123	
3.000	597.1	.0102	11.1	.0101	.0102
	994.7	.0103	6.69	.0102	

These results and those in the previous paper can be calculated to mole fractions or molalities with an accuracy within that of the measurements by using the densities for potassium chloride solutions as given in the "International Critical Tables."

Figure 1 shows graphically the change of the solubility of molecular benzoic acid with the nature and concentration of the solvent electrolyte. With our values at 25.15° are shown those of Hoffmann and Langbeck,⁴ and Freundlich and Seal⁵ at 25° in potassium chloride solutions. Their solutions were not buffered and their determinations give only the total solubility of the benzoic acid. We have calculated the ionized part from

⁴ Hoffmann and Langbeck, *Z. physik. Chem.*, **51**, 385 (1905).

⁵ Freundlich and Seal, *Kolloid-Z.*, **11**, 257 (1912).

our values of the classical dissociation constant and have subtracted that part from their values. As the plot shows, the agreement is good. The values of Berry⁶ in potassium chloride and sodium chloride solutions at 20° are shown with those of Güntelberg and Schiödt⁷ at the same temperature. Finally the values obtained by Larsson at 18° are shown for potassium chloride and sodium benzoate solutions.⁸ Larsson finds a decidedly opposite effect for sodium benzoate, that is to say, the solubility of molecular benzoic acid is increased by the solvent salt, sodium benzoate.⁹ The effect of sodium benzoate is noticeable in our buffers but is probably less than 1% for the benzoate ion concentrations used. It does, however, emphasize the dependence of the electrolyte effect upon the individual nature of the solvent salt. For the solvent salts potassium chloride and sodium chloride the solubility of molecular benzoic acid decreases rapidly with increasing salt concentration. The effect is greater for sodium chloride than for potassium chloride.

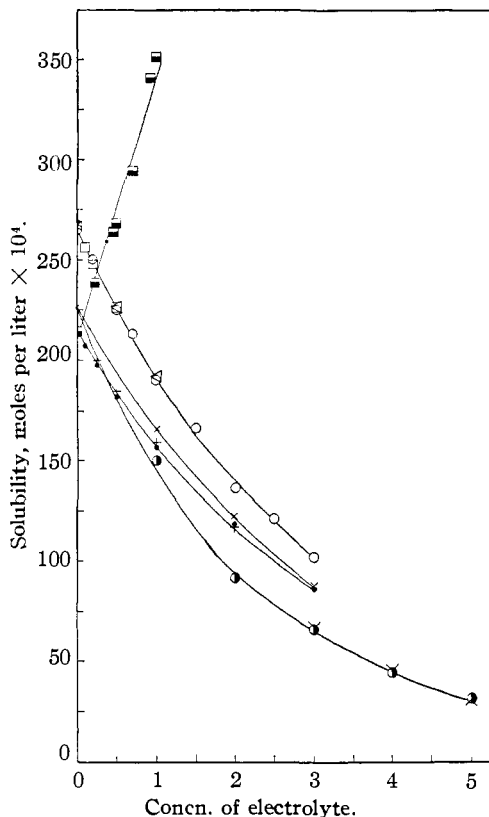
In Table II the classical dissociation constant, $K_c = C_{H^+} C_{B^-} / C_{HB}$ has been calculated from our determination of $C_{H^+} C_{B^-}$ by the electrometric and catalytic methods, and

⁶ These determinations were carried out by Mr. W. H. Berry with one of us (M. K., Jr.).

⁷ Güntelberg and Schiödt, *Z. physik. Chem.*, **135**, 393 (1928).

⁸ Larsson, *ibid.*, **148A**, 304 (1930).

⁹ Since this thesis was submitted Larsson has reported a number of salts which increase the solubility of benzoic acid. He has also investigated the effect of temperature on the activity coefficient of molecular benzoic acid. Larsson, *ibid.*, **153A**, 309, 466 (1931).



In KCl: ○, K. + C.; ◁, F. + S.; ◻, H. + L. at 25°; ×, B. at 20°; +, ●, L. at 18°. In Na Benzoate: ◻, L. at 18°. In NaCl: ○, B. at 20°; ∇, △, G. + S. at 20°; ● unbuffered + buffered.

Fig. 1.—Solubility of molecular benzoic acid.

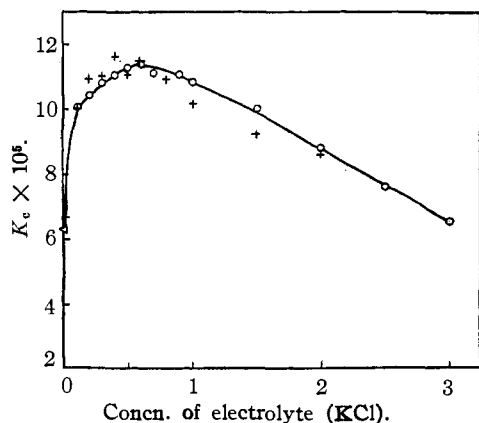
from the solubility of molecular benzoic acid in the solutions at each electrolyte concentration.

TABLE II
THE DISSOCIATION CONSTANT OF BENZOIC ACID IN POTASSIUM CHLORIDE SOLUTIONS AT 25.15°

KCl + NaB, moles per liter	$C_H + C_B$ $\times 10^3$, e. m. f.	$C_H + C_B$ $\times 10^3$, cat.	C_{HB} , moles per liter	K_a $\times 10^5$, cat.	K_c $\times 10^5$, e. m. f.
0.1	25.7	25.8	0.0255	10.12	10.08
.2	26.1	27.4	.0250	10.96	10.43
.3	26.1	26.8	.0241	11.12	10.83
.4	25.8	26.9	.0231	11.64	11.18
.5	25.5	24.9	.0225	11.07	11.32
.6	24.9	25.5	.0219	11.64	11.38
.7	23.7		.0213		11.12
.8		22.5	.0206	10.92	
.9	22.1		.0199		11.10
1.01	20.5	19.3	.0190	10.16	10.79
1.5	16.5	15.3	.0166	9.22	9.94
2.0	12.1	11.8	.0137	8.61	8.84
2.5	9.19		.0121		7.58
3.0	6.65		.0102		6.52

Figure 2 shows the change of the dissociation constant of the acid with increasing electrolyte concentration.

Table III gives the values of the dissociation constant obtained by Berry and by Güntelberg and Schiödt for potassium chloride and sodium chloride solutions.



○, E. m. f.; +, catalytic; ◁, conductivity.

Fig. 2.—Electrolyte effect on the dissociation constant of benzoic acid.

respectively. The values for the first dissociation constant of carbonic acid are from Güntelberg and Schiödt.⁷

¹⁰ Harned and Murphy, *THIS JOURNAL*, 53, 8 (1931).

¹¹ Harned and Owen, *ibid.*, 52, 5079 (1930).

TABLE III

COMPARISON OF K_c FOR BENZOIC ACID IN SODIUM AND POTASSIUM CHLORIDE SOLUTIONS

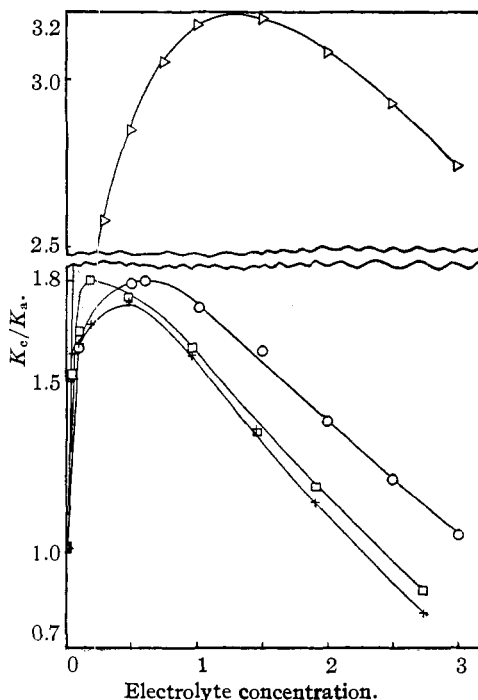
KCl + NaB, moles per liter	$C_{H^+} C_{B^-}$ $\times 10^7$, Berry, 20°	C_{HB} moles per liter, Berry, 20°	K_c $\times 10^5$, Berry, 20°	K_c $\times 10^5$, G. and S., 20°
1.0	16.9	0.0166	10.18	
2.0	9.81	.0123	7.98	
3.0	5.33	.0880	6.06	5.84
NaCl + NaB				
1.0	16.2	.01500	10.80	
2.0	8.61	.00918	9.38	
3.0	4.20	.00656	6.40	6.25
3.0	1.76	.00442	3.98	4.03
5.0	0.717	.00313	2.29	2.46

The curves for formic and acetic acids are similar, while that for carbonic acid is strikingly different, the maximum value of K_c for carbonic acid being over three times K_a . In general the K_c/K_a curve is different for different monobasic acids. These differences are attributed to two causes, the salting out effect on the ions and molecules and the interaction effect which depends on the deformability. Güntelberg and Schiödt⁷ have given an interesting discussion of the effect of these factors upon the dissociation constant of a given acid in different solvent salt solutions.

The change of the mean activity coefficient of the ions of benzoic acid with potassium chloride concentration as determined in a previous paper³ is given by the extended Debye-Hückel equation

$$-\log \sqrt{f_{H^+} f_{B^-}} = \frac{0.5 \sqrt{c}}{1 + \kappa b} + \beta c$$

where $\kappa = 0.33 \times 10^8 \sqrt{c}$, b is the apparent average ionic diameter, taken here as 5.15×10^{-8} cm., β is an empirical constant taken



All in KCl: \triangleright , carbonic acid, G. + S.; \circ , benzoic acid; $+$, acetic acid, H. + M.; \square , formic acid, H. + O.

Fig. 3.— K_c/K_a vs. electrolyte concentration.

equal to -0.139 , and c is the electrolyte concentration in moles per liter. Below we show that

$$\log f_{\text{HB}} = 0.138 c$$

Since

$$K_c = K_a \frac{f_{\text{HB}}}{f_{\text{H}^+} f_{\text{B}^-}}$$

we have

$$\log K_c = \log K_a + \log f_{\text{HB}} - \log f_{\text{H}^+} f_{\text{B}^-}$$

and substituting

$$\log K_c = \log K_a + 0.138 c + 2 \left[\frac{0.5 \sqrt{c}}{1 + 1.70 \sqrt{c}} + \beta c \right]$$

Taking $K_a = 6.31 \times 10^{-5}$, we have

$$\log K_c = -4.200 + \frac{\sqrt{c}}{1 + 1.70 \sqrt{c}} - 0.140 c$$

an equation which gives our values for K_c for solutions containing from 0.1 mole per liter to 3 moles per liter of potassium chloride within 2%.

Since all the solutions were saturated with benzoic acid, the activity of the molecular benzoic acid remained constant and equal to its solubility in pure water

$$a_{\text{HB}} = f_{\text{HB}} c_{\text{HB}}$$

the activity coefficient, f_{HB} , being set equal to one at zero electrolyte concentration. Upon subtracting the ionized part as calculated from conductivity measurements from the solubility of benzoic acid in water, and upon making a small correction for the ion concentration ($\mu = 0.0013$), a value of 0.02650 mole per liter is obtained.³ Thus

$$f_{\text{HB}} = \frac{0.02650}{c_{\text{HB}}}$$

The values of the activity coefficient calculated in this way are given in Table IV and for comparison we have included a summary of the results of Berry, Hoffmann and Langbeck, Güntelberg and Schiödt and Larsson.

An inspection of the table shows that for low electrolyte concentration the activity coefficient is practically independent of temperature over the range given.

Some of these values are shown graphically in Fig. 4, where the logarithm of the activity coefficient is plotted against the electrolyte concentration.

An equation of the form $\log f = kc$ expresses the results very well. For our results at 25.15° in potassium chloride solution

$$\frac{\log f}{c} = 0.138$$

For the results of Berry at 20° and of Güntelberg and Schiödt at 25° in sodium chloride solution

$$\frac{\log f}{c} = 0.176$$

TABLE IV
 COMPARISON OF VALUES OF f_{HB}

Electrolyte, KCl, moles per liter	Buffers, 25°	Hoffmann and Langbeck, 25°	Freundlich and Seal, 25°	Larsson, buffers, 18°	Larsson unbuff., 18°	G. and S. buff., 20°	Berry. buff., 0.02265
							$\frac{C_{HB}}{20}$
0	(1.00)	(1.00)	(1.00)	(1.00)	(1.00)	(1.00)	(1.00)
0.05		1.02					
.1	1.04	1.04			1.04		
.2	1.06	1.07					
.26				1.08	1.09		
.3	1.10						
.33		1.11					
.4	1.15						
.5	1.18	1.18	1.18	1.18	1.18		
.6	1.21						
.7	1.25						
.9	1.33						
1.01	1.40		1.39	1.37	1.37		1.37
1.5	1.60						
2.0	1.94			1.86	1.81		1.84
2.5	2.19						
3.0	2.61			2.57		2.55	2.58
NaCl							
0				(1.00)	(1.00)	(1.00)	(1.00)
0.25				1.11			
.5				1.23	1.24		
1.0				1.51	1.49		1.51
2.0				2.26	2.25		2.47
3.0				3.38	3.35	3.40	3.46
4.0						5.05	5.14
5.0						7.50	7.25

At 18° Larsson gives the values

$$k = 0.137 \text{ for KCl}$$

$$k = 0.177 \text{ for NaCl}$$

When the concentrations are expressed in moles per 1000 g. of water, and $\log \gamma$ is plotted against m , the points do not lie on a straight line as in Fig. 3. The best line which can be drawn, however, is represented by the equation

$$\log \gamma = 0.12 m$$

Using the data on the solubility of benzoic acid available at that time, Randall and Failey¹² gave $k = 0.13$ for potassium chloride and 0.18 for sodium chloride solution.

The activity coefficient of benzoic acid is larger in sodium chloride solution than in potassium chloride solution, that is to say, the solubility is less in sodium chloride than in potassium chloride solution of the same concentration. Since the salting out effect depends on the change in the

¹² Randall and Failey, *Chem. Reviews*, **4**, 291 (1927).

orientation of the water molecules toward the neutral molecule, one would expect the smaller sodium ion to have a greater effect than the larger potassium ion. This is in agreement with the facts and theory as discussed by Debye and McAulay¹³ and Scatchard and others.¹⁴ As pointed out by Scatchard, various Hofmeister series have been put forward for the cations and anions. Glasstone and Pound,¹⁵ who studied the electrolyte effect on the solubility of ethyl acetate, give the order $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$ and $\text{Cl}^- > \text{Br}^- > \text{I}^-$ for decreasing solubility of ethyl acetate. Linderström-Lang¹⁶ shows the same order for hydroquinone, quinone and succinic acid (uncorrected for the dissociated part).

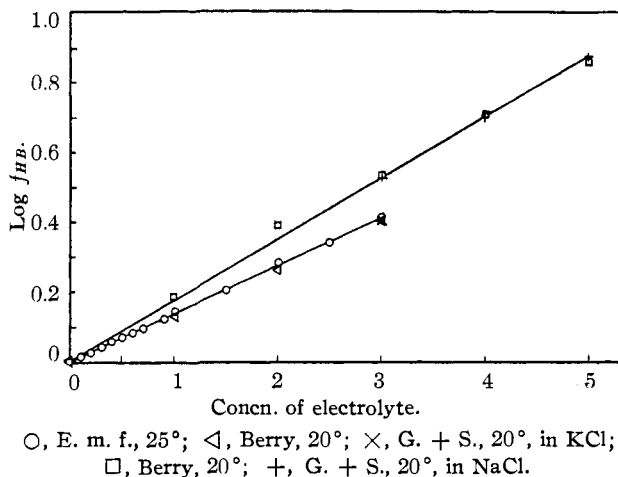


Fig. 4.—Activity coefficients of molecular benzoic acid in potassium chloride and sodium chloride solutions.

Haesseler¹⁷ finds the same general order for benzoic acid. Haesseler reports the solubility of total benzoic acid and has not corrected in any way for the part present as ions. Larsson demonstrated that the salting out of benzoic acid is, roughly speaking, an additive property of the ions of the solvent salt, *i. e.*

$$\log f = kc = [k_{\text{C}^+} + k_{\text{A}^-}]c$$

he arbitrarily set k_{K^+} equal to k_{Cl^-} , and calculated salting out constants for all the ions of the solvent salts studied.

In Table V we give some of Larsson's¹⁸ ionic salting out constants and in

¹³ Debye and McAulay, *Physik. Z.*, **24**, 185 (1923).

¹⁴ Scatchard, *Chem. Reviews*, **3**, 383 (1927).

¹⁵ Glasstone and Pound, *J. Chem. Soc.*, **127**, 2660 (1925).

¹⁶ Linderström-Lang, *Compt.-rend. trav. lab. Carlsberg*, **15**, 4 (1924).

¹⁷ Haesseler, Dissertation, Columbia University, 1929.

¹⁸ Larsson, *Z. physik. Chem.*, **153**, 299 (1931).

addition the radii of the ions as calculated by Pauling¹⁹ for crystals. While these radii will not necessarily be the same in solution they will probably have the same relative magnitudes.

TABLE V.
COMPARISON OF IONIC SIZE WITH SALTING OUT CONSTANT, k

Ion	Radius, Å.	k	Ion	Radius, Å.	k
Li ⁺	0.60	0.12	Mg ⁺⁺	0.65	0.10
Na ⁺	0.95	.11	Ca ⁺⁺	0.99	.10
K ⁺	1.33	.07	Sr ⁺⁺	1.13	.09
Rb ⁺	1.48	.02	Ba ⁺⁺	1.35	.08
Cs ⁺	1.69	-.08	Cl ⁻	1.81	0.07
			Br ⁻	1.95	0.00
			I ⁻	2.16	-0.02

From Table V it appears that k decreases with increasing ion size. In order to go further with any theoretical discussion, one would have to have information as to the change in dielectric constant and freezing points of these solutions, as pointed out by Debye and McAulay and Scatchard, as well as some knowledge of the deformability of the ions and molecules. Larsson points out that his results are qualitatively in agreement with the available dielectric data. The further study of the solubility of molecular benzoic acid in salt solutions offers a number of interesting possibilities, especially in view of the increase of solubility of benzoic acid in solutions of sodium benzoate ($k = -0.21$) and a number of other salts such as sodium β -naphthalene sulfonate ($k = -0.75$).

Summary

1. The solubility at 25.15° of benzoic acid in potassium chloride solutions has been determined and from determinations of the hydrogen-ion concentrations of these solutions the solubility of molecular benzoic acid has been calculated.

2. From these solubility values and the values of the ion product $C_{H^+} C_{B^-}$, the classical dissociation constant of benzoic acid has been calculated at the various electrolyte concentrations from 0.1 to 3.0 moles per liter.

3. A comparison of the change of the dissociation constant with electrolyte concentration has been given for different acids in the same solvent salt.

4. The activity coefficient of molecular benzoic acid in potassium chloride solutions has been evaluated. The results are expressed by the equation $\log f = 0.138c$.

5. A discussion of the relation of ion size to salting out has been given.

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¹⁹ Pauling, THIS JOURNAL, 49, 765 (1927).