alyzed by an aluminum halide and a halogen acid. This is substantiated by more recent work, which showed that the halide acid was essential to these isomerizations, and also by the fact that the aromatic products which are the strongest bases are favored. This cation, ArH+, has not been identified in the aluminum halide–halogen acid catalyst systems since the reactions are usually carried out in a neutral or aromatic medium where the equilibrium

$$\mathrm{Ar} + \mathrm{HX} \rightleftarrows \mathrm{ArH}^+ + \mathrm{X}^- \qquad (11)$$

would be almost entirely to the left, and where the low dielectric constant of the solvent would not favor the formation of ionic intermediates in appreciable concentration.

The recent work of Brown and Pearsall[8] tends to substantiate this viewpoint. They postulate that when the complex phase appears in a Friedel–Crafts type reaction, the formation of ionic intermediates is facilitated. This accounts for the greatly increased rate of reaction as soon as this second phase appears. Since this paper was submitted, Brown and Brady have given a more detailed presentation of their viewpoint.[19]

Acknowledgment.—The authors are indebted to D. A. McCaulay of Standard Oil Company of Indiana for supplying us with many of the methylbenzenes used.

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CHICAGO 16, ILL.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA AND THE DEPARTMENT OF CHEMISTRY OF ILLINOIS INSTITUTE OF TECHNOLOGY]

The Dissociation Constants of Acids in Salt Solutions. I. Benzoic Acid

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RECEIVED AUGUST 4, 1952

With the increased use of the "swamping-salt" principle for kinetic and equilibrium studies, experimental determinations of the dissociation constants of acids in various solvent salts are needed. The present paper reports the dissociation constant of benzoic acid in water for three solvent salts and the dissociation constant in methyl and ethyl alcohol and ethylene glycol for the solvent salt lithum chloride.

In connection with kinetic and acid strength studies in the author's laboratory, many determinations of the dissociation constant of benzoic acid in aqueous and non-aqueous salt solutions have been accumulated. This paper presents a summary of these results together with a calculation of the activity coefficients.

Most of the measurements were made with the cell

$$\begin{array}{c|ll||l||ll|c} & \mathrm{HB} & 0.005\,M & & \mathrm{HCl} & 0.005\,M & \\ \mathrm{Au} & \mathrm{MB} & 0.005\,M & \mathrm{MCl}\ 1.00\,M & \mathrm{MCl} & X\,M & \mathrm{Au} \\ & \mathrm{MCl} & X\,M & & & & \\ & \multicolumn{2}{c}{\text{Quinhydrone}} & & \multicolumn{2}{c}{\text{Quinhydrone}} & \end{array}$$

where $X \geqq 0.045M$

as reported by Elliott and Kilpatrick,[2] while the others were made with a similar cell described by Kilpatrick and Chase.[3] Within the assumptions involved, the electromotive force method gives the ratio of the hydrogen ion concentrations in the two halves of the cell, and if we assume that the hydrogen ion concentration is equal to the stoichiometric concentration of the strong acid, the usual concentration dissociation constant can be calculated from the known stoichiometry of the buffer solution

$$K_c = C_{\mathrm{H_3O^+}}\frac{C_{\mathrm{B^-}}}{C_{\mathrm{HB}}} \qquad (1)$$

where the concentration of water is included in the constant. Table I summarizes the results for the aqueous salt solutions of alkali chlorides. Since

$$K_a = K_c\frac{f_{\mathrm{H^+}}f_{\mathrm{B^-}}}{f_{\mathrm{HB}}} \qquad (2)$$

and $K_a = 6.32 \times 10^{-5}$,[4] and the salting-out constants for benzoic acid are known,[5] the mean activity coefficient of the ions of benzoic acid can be calculated. The ratio K_c/K_a, the activity coefficient of molecular benzoic acid f_{HB}, and the mean activity coefficient of the ions of benzoic acid $\sqrt{f_{\mathrm{H^+}}\,f_{\mathrm{B^-}}}$ are given in Table II.

TABLE I

THE DISSOCIATION CONSTANT OF BENZOIC ACID IN AQUEOUS SALT SOLUTIONS AT 25°, $K_c \times 10^5$

Moles/liter	Electrolyte KCl	NaCl	LiCl
0.05	9.10	9.12	9.16
.10	10.08	10.05	11.08
.20	10.43	10.81	11.47
.30	10.83	11.38	11.86
.40	11.18	11.79	12.93
.50	11.32	11.90	12.95
.60	11.38	11.85	13.00
.70	11.12	11.80	12.95
.80	11.06	11.72	12.94
.90	11.10	11.55	12.90
1.00	10.79	11.36	12.88
1.50	9.94	10.48	12.60
2.00	8.84	9.20	11.25
2.50	7.58	7.58	9.46
3.00	6.52	6.49	8.99

Table III presents the dissociation constant of benzoic acid in the solvents methyl and ethyl alcohol and ethylene glycol, at total ion concentrations of 0.05 and 0.10 molar for LiCl from e.m.f. measurements against HCl in the same solvent salt. The values for the dissociation constant at zero electro-

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[3] M. Kilpatrick and E. F. Chase, THIS JOURNAL, **53**, 1732 (1931).

[4] F. G. Brockman and M. Kilpatrick, *ibid.*, **56**, 1483 (1934).

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TABLE II

THE ACTIVITY COEFFICIENTS OF BENZOIC ACID IN AQUEOUS SALT SOLUTIONS AT 25°

Electrolyte Moles/liter	KCl K_c/K_a	KCl f_{HB}	KCl $\sqrt{f_{H^+}f_{B^-}}$	NaCl K_c/K_a	NaCl f_{HB}	NaCl $\sqrt{f_{H^+}f_{B^-}}$	LiCl K_c/K_a	LiCl f_{HB}	LiCl $\sqrt{f_{H^+}f_{B^-}}$
0.05	1.44	1.02	0.84	1.45	1.02	0.84	1.45	1.02	0.84
.10	1.60	1.03	.80	1.59	1.04	.81	1.76	1.05	.77
.20	1.65	1.07	.80	1.71	1.08	.79	1.82	1.09	.77
.30	1.72	1.10	.80	1.80	1.13	.79	1.88	1.14	.78
.40	1.77	1.14	.80	1.87	1.20	.80	2.05	1.19	.76
.50	1.79	1.17	.81	1.89	1.23	.81	2.05	1.25	.78
.60	1.80	1.21	.82	1.88	1.28	.83	2.06	1.30	.79
.70	1.76	1.25	.84	1.87	1.33	.84	2.05	1.36	.81
.80	1.75	1.29	.86	1.86	1.39	.86	2.05	1.43	.84
.90	1.76	1.33	.87	1.83	1.44	.87	2.05	1.49	.85
1.00	1.71	1.37	.90	1.80	1.50	.91	2.04	1.57	.86
1.50	1.58	1.61	1.01	1.66	1.84	1.05	2.00	1.94	.99
2.00	1.40	1.89	1.16	1.46	2.26	1.25	1.78	2.42	1.37
2.50	1.20	2.21	1.36	1.20	2.77	1.52	1.50	3.02	1.42
3.00	1.03	2.59	1.58	1.03	3.40	1.82	1.43	3.77	1.62

TABLE III

THE DISSOCIATION CONSTANT OF BENZOIC ACID IN ALCOHOLS

T, 25°; solvent salt, LiCl

Electrolyte Moles/liter	CH_3OH $10^{10}K_c$	CH_3OH K_c/K_a	C_2H_5OH $10^{10}K_c$	C_2H_5OH K_c/K_a	$(CH_2OH)_2$ $10^{10}K_c$
0	4.20	1.00	0.87	1.00	...
.05	20.8	4.95	13.8	15.9	225
.10	37.8	9.00	39.0	44.8	446

lyte concentration are chosen as follows. For methyl alcohol a recalculation of the conductance data of Goldschmidt and Aas[6] on salicylic acid, correcting for mobility changes and activity coefficients, yields 1.43×10^{-8} as compared to the reported value of 1.32×10^{-8}. The ratio of the dissociation constants of salicylic to benzoic acid in methyl alcohol is 34.0,[7] yielding 4.20×10^{-10} for the dissociation constant of benzoic acid at zero electrolyte concentration. For ethyl alcohol the conductance data for *p*-nitrobenzoic acid[8] seemed more consistent than those for benzoic acid which were reported at a water content of 3%. Similar calculations yield 1.64×10^{-9} for the thermodynamic dissociation constant of *p*-nitrobenzoic acid and 8.70×10^{-11} for benzoic in ethyl alcohol, the ratio of the dissociation constants being taken as 18.9.[9] No value of the thermodynamic dissociation constant is available in the solvent ethylene glycol.

Discussion of Results

In aqueous solutions the ratio of the dissociation constant in a particular salt solution to the thermodynamic dissociation constant increases in the order KCl < NaCl < LiCl. As shown in Table II this is due to the difference in the activity coefficients of molecular benzoic acid as well as the difference in the mean activity coefficient of the ions. In applying the "swamping-salt" principle it is well to note that the assumption that the activity coefficients are constant for constant salt concentration applies for the particular solvent salt and data obtained in one solvent salt are not applicable to another. For example, the K_c/K_a ratio for benzoic acid in KCl at one molar concentration is 1.71, for NaCl 1.80 and for LiCl 2.04. The differences will be less apparent at lower concentrations in aqueous solutions, but the magnitude of the change is so much greater in the alcohols that it should be borne in mind that the K_c/K_a ratios given are only for the solvent salt lithum chloride. The K_c/K_a ratio for 0.10 LiCl increases from 1.76 to 9.00 to 44.8 for the solvents water, methyl and ethyl alcohol. Very few data have been accumulated over a temperature range, but our conductivity measurements indicate little change in the dissociation constant in the range 20 to 35°. Recent measurements of cells without liquid junction[10] give 6.13, 6.12, 6.09 and 6.01×10^{-5} for the dissociation constant at infinite dilution at 20, 25, 30 and 35°. These values are lower than those more recently reported by Jones and Parton[11] as 6.237, 6.295, 6.266 and 6.237×10^{-5} at 20, 25, 30 and 35°. On a volume concentration scale the above value at 25° is 6.28×10^{-5} to be compared with 6.32[4] and 6.29[12] by conductance measurements. Calculations of the earlier data of Schaller[13] place the maximum in the thermodynamic dissociation constant at 27°. The fact that there is very little change of the dissociation constant over the range 20–35° makes it a suitable reference acid.

Acknowledgment.—The author wishes to acknowledge the use of the experimental results of his former students F. G. Brockman, E. F. Chase, R. D. Eanes and J. H. Elliott at the University of Pennsylvania, and J. G. Morse at the Illinois Institute of Technology.

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