[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. II. Acetic Acid

BY MARTIN KILPATRICK AND R. DEAN EANES

RECEIVED AUGUST 4, 1952

The dissociation constant of acetic acid is determined with benzoic acid and the solvated proton as the reference acid in salt solutions of the alkali halides.

The dissociation constant of acetic acid in salt solutions was determined by two sets of measurements, the first being against the reference acid the solvated proton, as described in paper one of the series,[1] and the second by measurement of the cell.

Au	HAc 0.005 M MAc 0.005 M MCl X M	MCl 1.00 M	HB 0.005 M MB 0.005 M MCl X M	Au
	Quinhydrone		Quinhydrone	

which after suitable small corrections for the change in buffer ratios gives directly the equilibrium constant for the reaction

$$HAc + B^- \rightleftharpoons HB + Ac^- \qquad (1)$$

where

$$K_{A_xB_0} = \frac{(Ac^-)}{(HAc)} \times \frac{(HB)}{(B^-)} \qquad (2)$$

and $K_{A_xB_0}$ is the ratio of the dissociation constant of acetic acid to that of benzoic acid.

Column II of Table I gives the values of this ratio for aqueous solutions of potassium, sodium and lithium chloride. Column III gives the dissociation constant of acetic acid calculated from the dissociation constant of benzoic acid in the corresponding salt solutions. Column IV gives the results of the measurements against hydrochloric acid while columns V and VI give the results of Harned and Murphy[2] and Harned and Hickey[3,4] from measurements of cells without liquid junction.

TABLE I

DISSOCIATION CONSTANT OF ACETIC ACID AT 25°

Electrolyte, moles/liter Reference acid →	$K_{A_xB_0}$ Benzoic	$K_c \times 10^5$ Benzoic	Hydrochloric			K_c/K_a
			Potassium chloride			
0.05	0.285	2.59[a]	2.65[b]	2.57[c]	2.57[d]	1.48[e]
.10	.280	2.82	2.81	2.79	2.84	1.61
.20	.277	2.89	3.03	2.99	3.10	1.65
.30	.276	2.99	3.12	3.07	3.21	1.70
.40	.273	3.05	3.17	3.09	3.27	1.74
.50	.269	3.05	3.20	3.08	3.28	1.74
.60	.267	3.04	3.12	3.07	3.25	1.73
.70	.263	2.93	3.14	3.01	3.21	1.67
.80	.261	2.89	2.99	2.95	3.13	1.65
.90	.257	2.85	2.85	2.88	3.06	1.63
1.00	.255	2.75	2.80	2.81	2.97	1.57
1.50	.246	2.45	2.41	2.37	2.46	1.39
2.00	.237	2.10	1.99	1.91	1.95	1.19
2.50	.227	1.72	1.62	1.56	..	0.98
3.00	.219	1.43	1.31	1.27	..	0.81
			Sodium chloride			
0.05	0.278	2.54	2.50	2.83	2.55	1.45
.10	.278	2.79	2.77	2.96	2.77	1.59
.20	.276	2.98	3.03	3.11	3.00	1.70
.30	.276	3.14	3.25	3.21	3.14	1.79
.40	.275	3.24	3.25	3.27	3.26	1.85
.50	.275	3.27	3.27	3.32	3.31	1.87
.60	.273	3.24	3.33	3.29	3.30	1.84
.70	.271	3.20	3.23	3.25	3.27	1.82
.80	.265	3.11	3.15	3.19	3.21	1.77
.90	.265	3.06	3.25	3.11	3.15	1.75
1.00	.263	2.99	3.15	3.03	3.09	1.70
1.50	.260	2.73	2.76	2.60	2.77	1.55
2.00	.251	2.31	2.38	2.18	2.43	1.32
2.50	.245	1.86	1.97	1.76	2.07	1.06
3.00	.242	1.57	1.71	1.45	1.68	0.90
			Lithium chloride			
0.05	0.287	2.63	2.62		2.61	1.50
.10	.285	3.16	3.17		2.90	1.80
.20	.286	3.28	3.26		3.10	1.87
.30	.286	3.39	3.56		3.21	1.93
.40	.284	3.67	3.69		3.27	2.09
.50	.280	3.63	3.63		3.30	2.07
.60	.278	3.61	3.63		3.27	2.06
.70	.277	3.59	3.58		3.24	2.05
.80	.277	3.58	3.61		3.18	2.04
.90	.281	3.63	3.62		3.10	2.07
1.00	.281	3.62	3.69		3.00	2.06
1.50	.282	3.55	3.48		2.51	2.03
2.00	.283	3.18	3.20		2.02	1.82
2.50	.284	2.69	2.81		..	1.52
3.00	.287	2.58	2.61		..	1.47

[a] Based on K_c values from paper I.[1] [b] Results this Laboratory. [c] Results of Harned and Murphy.[2] [d] Results of Harned and Hickey.[3,4] [e] K_c from column 3, $K_a = 1.754 \times 10^{-5}$.[5]

The agreement between columns III and IV is as good as the agreement between V and VI. Column VII gives the activity coefficient factor F for acetic acid in the salt solution from the relationship

$$\frac{K_c}{K_a} = F = \frac{f_{HAc}}{f_{H^+}f_{Ac^-}} \qquad (3)$$

where $K_a = 1.754 \times 10^{-5}$.[5] In this case f_{HAc} is not known so that the product of the activity coefficients of the ions cannot be separately evaluated.

The change of the equilibrium constant for the isoelectric reaction of equation (1) with electrolyte concentration is different for the three electrolytes. The data can be represented by the equation

$$\log K_{A_xB_0} = \bar{1}.441 + BC$$

where C represents the concentration in moles per liter, B has the values -0.033, -0.020 and 0.006

(1) M. Kilpatrick, THIS JOURNAL, **75**, 584 (1953).
(2) H. S. Harned and G. Murphy, *ibid.*, **53**, 8 (1931).
(3) H. S. Harned and F. C. Hickey, *ibid.*, **59**, 1284 (1937).
(4) H. S. Harned and F. C. Hickey, *ibid.*, **59**, 2303 (1937).
(5) H. S. Harned and R. W. Ehlers, *ibid.*, **55**, 652 (1933).

for the chlorides of potassium, sodium and lithium. The logarithm of the ratio of the dissociation constants at infinite dilution from conductance data is $\bar{1}.441$. The agreement between the observed values of log $K_{A_xB_0}$ and those calculated by equation 4 is poorer for the points below 0.5 M.

Table II gives the dissociation constant of acetic acid in methyl and ethyl alcohol and ethylene glycol. The K_c/K_a ratios are in accord with the results for benzoic acid in the same solvents.

TABLE II

THE DISSOCIATION CONSTANT OF ACETIC ACID IN ALCOHOLS

T, 25°; solvent salt, LiCl

Electrolyte, mole/liter	CH_3OH $K_{A_xB_0}$	CH_3OH 10^{10} K_c	K_c/K_a	C_2H_5OH $K_{A_xB_0}$	C_2H_5OH 10^{10} K_c	K_c/K_a	$(CH_2OH)_2$ $K_{A_xB_0}$	$(CH_2OH)_2$ 10^{10} K_c
0	0.576	2.42	1.00	0.680	0.592		...	
0.05	.573	13.2	5.46	.680	9.40	15.9	0.447	101
.10	.580	21.9	9.05	...			...	

CHICAGO, ILLINOIS

[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. III. Glycolic Acid

BY MARTIN KILPATRICK AND R. DEAN EANES

RECEIVED AUGUST 22, 1952

The dissociation constant of glycolic acid has been determined in salt solutions using acetic, benzoic and the solvated proton as reference acids.

The equilibrium constants for the reaction

$$HG + B_0 \rightleftharpoons A_0 + G^- \quad (1)$$

where HG represents glycolic acid and A_0 represents the reference acid, have been determined by the experimental method given in papers I[1] and II[2] of this series.

The results are summarized in Table I for the reference acids, benzoic, acetic and the solvated proton. The agreement between the experimental results is satisfactory. Extrapolation of the values for the equilibrium constant of equation (1) to infinite dilution yields 1.51 and 1.45×10^{-4} for the dissociation constant of glycolic acid on the basis of 6.32×10^{-5} for benzoic acid and 1.745×10^{-5} for acetic acid. The values in the literature for the dissociation constant of glycolic acid are 1.475[3] and 1.54×10^{-5}.[4]

TABLE I

DISSOCIATION CONSTANTS OF GLYCOLIC ACID AT 25°

Electrolyte moles/liter Reference acid →	$K_{A_xB_0}$ Benzoic	$K_c \times 10^4$ Benzoic	$K_{A_xB_0}$ Acetic	$K_c \times 10^4$ Acetic	$K_c \times 10^4$ Hydrochloric	K_c/K_a
Lithium chloride						
0.05	2.47	2.26[a]	8.40	2.21[b]	2.34	1.50[c]
.10	2.39	2.65	8.47	2.68	2.62	1.82
.20	2.64	3.03	8.52	2.79	2.77	1.89
.30	2.50	2.97	8.57	2.91	2.99	1.97
.40	2.60	3.36	8.59	3.15	3.03	2.14
.50	2.56	3.32	8.63	3.13	3.05	2.12
.60	2.54	3.30	8.64	3.12	3.12	2.12
.70	2.51	3.25	8.66	3.11	3.13	2.11
.80	..		8.61	3.08	3.19	2.09
.90	..		8.77	3.18	3.25	2.16
1.00	2.53	3.26	8.83	3.20	3.21	2.17
1.50	2.54	3.20	9.05	3.21	3.13	2.18
2.00	..		9.60	3.05	3.06	2.07
2.50			10.51	2.83	2.99	1.92
3.00			10.75	2.77	2.85	1.88
Sodium chloride						
0.05	2.43	2.22	8.36	2.12	2.04	1.44
.10	2.43	2.44	8.35	2.33	2.26	1.58
.20	2.52	2.42	8.42	2.51	2.58	1.70
.30	2.48	2.82	8.53	2.67	2.70	1.81
.40	2.52	2.97	8.51	2.76	2.71	1.87
.50	2.53	3.01	8.65	2.83	2.86	1.92
.60	2.52	2.99	8.52	2.76	2.94	1.87
.70	2.50	2.95	8.75	2.80	2.82	1.90
.80	2.53	2.97	8.82	2.74	2.84	1.86
.90	2.52	2.91	8.83	2.70	2.86	1.83
1.00	2.54	2.89	8.97	2.68	2.82	1.82
1.50	2.53	2.65	9.38	2.56	2.58	1.74
2.00	2.60	2.39	9.82	2.27	2.33	1.54
2.50	2.63	1.99	10.1	1.88	1.98	1.27
3.00	2.68	1.74	10.4	1.63	1.80	1.10
Potassium chloride						
0.05			8.29	2.15	2.20	1.46
.10			8.07	2.28	2.38	1.55
.20			8.39	2.43	2.55	1.65
.30			8.48	2.54	2.64	1.72
.40			8.53	2.60	2.68	1.76
.50			8.70	2.65	2.72	1.80
.60			8.75	2.66	2.72	1.80
.70			8.69	2.55	2.70	1.73
.80			8.79	2.54	2.68	1.72
.90			8.79	2.51	2.53	1.70
1.00			8.82	2.43	2.51	1.65
1.50			9.12	2.23	2.20	1.51
2.00			9.20	1.93	1.86	1.31
2.50			9.30	1.60	1.53	1.08
3.00			9.45	1.35	1.21	0.92

[a] Based on K_c values from paper I.[1] [b] Based on K_c values from paper II.[2] [c] K_c from column 5; $K_a = 1.475 \times 10^{-4}$.

CHICAGO, ILL.

(1) M. Kilpatrick, THIS JOURNAL, **75**, 584 (1953).

(2) M. Kilpatrick and R. D. Eanes, *ibid.*, **75**, 586 (1953).

(3) L. F. Nims, *ibid.*, **58**, 987 (1936).

(4) J. Böeseken and H. Kalshoven, *Rec. trav. chim.*, **37**, 130 (1918).