[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

Salt Action on the Ionization of Acetic Acid and Hydrolysis of the Acetate Ion

BY HERBERT S. HARNED AND FREDERICK C. HICKEY, O.P.

From measurements of the electromotive forces of the cells

$$H_2 \mid HAc(M),\ MCl_n(m) \mid AgCl\text{–}Ag \qquad (1)$$

we[1] have determined the ionization of acetic acid in sodium chloride solutions from 0 to 40°. By combining with suitable data, we[2] computed also the concentration and activity coefficient terms of the hydrolytic reaction

$$Ac^- + H_2O \rightleftarrows HAc + OH^- \qquad (2)$$

Electromotive forces of these cells containing lithium, potassium and barium chlorides at 25° and at 0.2 and 0.5 M acetic acid have been obtained. From these, the following quantities have been derived: (1) the value k_A, or $m_H m_{Ac}/m_{HAc}$ in the salt solutions. Since the thermodynamic equation for the ionization of acetic acid is

$$K_A = \gamma_A^2 k_A \qquad (3)$$

and since the ionization constant, K_A, is known, the ionic activity coefficient product, γ_A^2, may be computed. (2) Upon combining this information with our knowledge of the ionization of water, $m_H m_{OH}$, in the salt solutions,[3-5] we have computed the quantities K_h, k_h, and γ_h in the thermodynamic equation of the hydrolytic reaction, or

$$K_h = \frac{\gamma_{HAc}\gamma_{OH}}{\gamma_{Ac}\gamma_{H_2O}} \ \frac{m_{HAc}m_{OH}}{m_{Ac}} = \gamma_h^2 k_h \qquad (4)$$

Either γ_h or k_h is a measure of the salt effect on the hydrolytic reaction.

Experimental Results and Derived Quantities

The observed results are given in Table I. Since the methods of computing results of this type have been discussed in detail by Harned and Owen[6] and by us,[1] we have simply given the values of k_A and k_h in Table II without mention of the intermediate steps. The necessary data for the computation of lithium, potassium and barium chlorides are to be found in the contributions of Harned and Copson,[4] Harned and Hamer,[3] and Harned and Geary,[5] respectively.

TABLE I

ELECTROMOTIVE FORCES OF THE CELLS AT 25°

$H_2 \mid HAc(M),\ MCl_n \mid AgCl\text{–}Ag$

$HAc = CH_3COOH$; M = Li; K, Ba

Li			K			Ba		
M	m	E	M	m	E	M	m	E
0.2020	0.0995	0.44811	0.2111	0.1004	0.44840	0.2022	0.03367	0.45866
.2021	.2031	.43030	.2123	.2020	.43163	.2004	.06672	.44221
.1973	.2938	.42105	.2107	.3006	.42253	.2016	.1016	.43205
.2003	.5053	.40609	.2108	.5019	.41049	.2021	.1684	.41914
.1999	.9983	.38481	.2120	1.0093	.39321	.2023	.3376	.40044
.2005	2.0031	.35691	.2114	2.0126	.37528	.2029	.6764	.37904
.5014	0.1003	.43532	.4862	0.1003	.43699	.2041	1.0201	.36381
.5012	.5009	.39380	.4846	0.5000	.39885	.5065	0.03377	.44601
.5013	1.0025	.37213	.4846	1.0000	.38206	.5038	.1680	.40658
			.4861	2.0062	.36332	.5016	.5015	.37635
						.5002	.9982	.35238

The values of a, the mean distance of approach of the ions, found most satisfactory for the extrapolation according to equation (8) in our earlier communication,[1] were 3.6 Å. for potassium

TABLE II

VALUES OF k_A AND k_h

$k_A = K_A$; $k_h = K_H$ when $\mu = 0$. $t = 25°$

	$k_A \times 10^5$			$k_h \times 10^{10}$		
μ	LiCl	KCl	BaCl₂	LiCl	KCl	BaCl₂
0.0	1.754	1.754	1.754	5.74	5.74	5.74
.02	2.290	2.302	2.292	5.81	5.77	5.83
.03	2.401	2.415	2.404	5.83	5.74	5.85
.06	2.630	2.650	2.635	5.93	5.69	5.96
.11	2.874	2.891	2.885	6.08	5.65	6.05
.21	3.167	3.151	3.190	6.27	5.61	6.29
.51	3.546	3.340	3.609	6.53	5.65	6.81
1.01	3.670	3.071	3.799	6.87	5.57	7.43
2.01	3.432	2.182	3.680	7.13	5.85	8.28
3.01	...	...	3.367	..	..	9.02

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[1] Harned and Hickey, THIS JOURNAL, **59**, 1284 (1937).

[2] Harned and Hickey, *ibid.*, **59**, 1289 (1937).

[3] Harned and Hamer, *ibid.*, **55**, 2194 (1933).

[4] Harned and Copson, *ibid.*, **55**, 2206 (1933).

[5] Harned and Geary, *ibid.*, **59**, 2032 (1937).

[6] Harned and Owen, *ibid.*, **52**, 5079 (1930).

and barium chlorides, and 4.0 Å. for the lithium chloride solutions. 1.754 × 10^{-5}[7] and 1.008 × 10^{-14}[3,4,5] were used for the ionization constants of acetic acid and water, respectively.

Observation of the results in Table II shows that the salt effects on the ionization of acetic acid verify the order found from less accurate results and a less refined method by Harned and Robinson.[8] The order of effect is: $k_A(BaCl_2) > k_A(LiCl) > k_A(NaCl) > k_A(KCl)$ in the concentrated solutions which is the reverse of that found for the activity coefficient of a strong electrolyte, such as hydrochloric acid in these salt solutions.

The variation of the concentration term of the hydrolytic reaction, k_h, with salt concentration is large in lithium and barium chloride solutions. The maximum effect produced by the salt at an ionic strength of 2.01 is approximately 20% in the case of lithium chloride and 30% in the case of barium chloride. Potassium chloride causes a small salt effect at 25° which is of the order of magnitude of the effect of sodium chloride.[2] The maximum variation of k_h, or the deviation from the law of mass action, is about 4%.

Summary

1. From the electromotive forces of the cells

$$H_2 \mid HAc(M),\ MCl_n(m) \mid AgCl\text{-}Ag$$

the ionization, k_A, of acetic acid in lithium, potassium, and barium chloride solutions at 25° has been determined.

2. By combining these results with information derived from the cells

$$H_2 \mid MOH(m_0),\ MCl_n(m_0), \mid AgCl\text{-}Ag$$

the salt effect on the hydrolytic reaction

$$Ac^- + H_2O \rightleftarrows HAc + OH^-$$

have been investigated. The concentration term, $m_{HAc}m_{OH}/m_{Ac}$, in the salt solutions has been computed. Its variation with salt concentration is found to be large in the lithium and barium chloride solutions. In potassium and sodium chloride solutions, however, the total variation from 0 to 3 μ is less than 4% at 25°.

NEW HAVEN, CONN. RECEIVED SEPTEMBER 8, 1937

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(7) Harned and Ehlers, THIS JOURNAL, **55**, 652 (1933).

(8) Harned and Robinson, *ibid.*, **50**, 3157 (1928).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Ionic Activity Coefficient Product and Ionization of Water in Uni-univalent Halide Solutions—A Numerical Summary

BY HERBERT S. HARNED AND MELVIN A. COOK

As a result of a number of recent investigations, the activity coefficient product, $\gamma_H\gamma_{OH}/a_{H_2O}$, of water in solutions of potassium,[1] sodium,[2] lithium[3] chlorides, and potassium,[4] sodium[4] and lithium bromides[5] have been determined over considerable temperature and concentration ranges. These measurements also lead to the determination of the thermodynamic ionization constant of water, K, defined by the equation

$$K_w = \frac{\gamma_H\gamma_{OH}}{a_{H_2O}} m_H m_{OH} = \gamma_w^2 m_w^2 \qquad (1)$$

Since both K_w and γ_w have been evaluated, the ionization of water, $m_H m_{OH}$, in the salt solutions may be computed. Owing to the voluminous nature of results, complete tabulation was not made in these contributions. In order to render them available in an approximate form at least, we have calculated γ_w by the empirical equation

$$2 \log \gamma_w = \log \frac{\gamma_H\gamma_{OH}}{a_{H_2O}} = - \frac{-2u\sqrt{\mu}}{1 + A\sqrt{2\mu}} + B\mu + C\mu^{3/2} \qquad (2)$$

in which, $u = 1.8143 \times 10^6 (DT)^{-3/2}$; $A = a$ $35.57\ (DT)^{-1/2}$; $D = 78.54\ [1 - 0.00460\ (t - 25) + 0.0000088\ (t - 25)^2]$; and where B and C may be expressed by the linear equations

$$B = b_0 + b_1 t \qquad (3)$$

$$C = c_0 + c_1 t \qquad (4)$$

the constants of which are given in Table I. For

TABLE I

CONSTANTS OF EQUATIONS

	a	b_0	$b_1 \times 10^4$	c_0	$c_1 \times 10^4$	Δ av.
KCl	3.6	0.266	5.20	−0.0350	−4.88	0.0027
NaCl	3.6	.198	2.00	− .0085	−2.0	.0032
LiCl	3.6	.039	2.00	.0325	−4.0	.0025
KBr	4.2	.205	12.75	− .016	−9.0	.0022
NaBr	4.2	.157	6.75	.010	−6.57	.0035
LiBr	4.2	.000	0.000	.0475	−2.20	.0041

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(1) Harned and Hamer, THIS JOURNAL, **55**, 2194 (1933).

(2) Harned and Mannweiler, *ibid.*, **57**, 1873 (1935).

(3) Harned and Copson, *ibid.*, **55**, 2206 (1933).

(4) Harned and Hamer, *ibid.*, **55**, 4496 (1933).

(5) Harned and Donelson, *ibid.*, **59**, 1280 (1937).