The Standard E.m.f. of the Silver–Silver Chloride Electrode and the Degenerate Activity Coefficient of Chloride Ion in the System Ethanol–Water[1a]

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We wish to report a brief reinvestigation of the

$$\text{Pt–H}_2\text{ (g, 1 atm.)/HCl}(c)\text{/AgCl–Ag} \qquad (1)$$

cell in the system ethanol–water at 25.0°. Our results are as follows.

(1) We have confirmed Anderson's discovery[2] that the irreversible formation of hydrochloric acid according to

$$2\text{AgCl(s)} + \text{H}_2\text{(g)} \longrightarrow 2\text{H}^+\text{Cl}^- + 2\text{Ag(s)} \qquad (2)$$

may occur in the cell at an appreciable rate and cause serious error at low concentrations. In our most extreme example, the normality of an aqueous hydrochloric acid solution increased from 0.00185 to 0.00213 after one weeks' exposure to hydrogen. For solutions at least 0.001 N in acid, the concentration change due to reaction 2 may be kept within 0.2% during the period required for e.m.f. measurement if the cell is equilibrated with hydrogen before immersing the Ag–AgCl electrode into the solution. By use of this technique, our results were within 0.1 mv. of values reported by Anderson at low concentrations,[2] and within 0.05 mv. of accepted values[3] in the range $0.05 > c > 0.005$ N.

(2) We have checked the old e.m.f. data of Harned and Fleyscher[4] in 50 mole % ethanol, taking care to avoid reaction 2. The two sets of data are compared in Fig. 1, where values of $E + 0.11831$ $(\log c - 1.600\sqrt{c})$ are plotted *vs.* c. Within the experimental precision, all data fall on a single line, except for the older value at the very lowest concentration (0.002 m). This value seems to be too low by about 1.3 mv., suggesting that the acid concentration in this cell might have increased significantly due to reaction 2. The accuracy of the older data has therefore been confirmed within the experimental precision at all concentrations above 0.004 N.

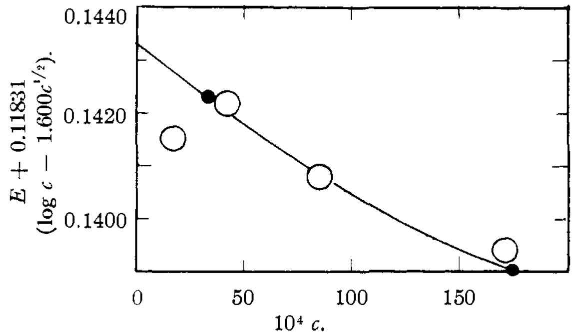

Fig. 1.—Open circles, data of Harned and Fleyscher; filled circles, present work.

(3) We have recalculated the values of the standard e.m.f., E^0, for cell 1 from the available e.m.f. data,[4–7] using the accurate recent dielectric constants of Hall and Phillips[8] in the calculation of activity coefficients. In solvents containing up to 25 mole % ethanol, ion pair formation is negligible, and activity coefficients y are estimated from

$$\log y = -S\sqrt{c}/(1 + As\sqrt{c}) \qquad (3)$$

where S is the Debye–Hückel limiting slope, 10^{-8} $A = 50.30/D^{1/2}T^{1/2}$, and s, the ion size parameter, is treated as an adjustable constant. In solvents containing more than 25 mole % ethanol, ion pair formation is not negligible, and activity coefficients are calculated from the equation suggested by Marshall and Grunwald[9]

$$\log y = \log \alpha - \frac{S\sqrt{\alpha c}}{(1 + 2.303S\sqrt{\alpha c})^{2/3}} + \frac{Bs^3\alpha c}{(1 + As\sqrt{\alpha c})^{3/2}} \qquad (4)$$

In equation 4, $B = 43.84 \times 10^{20}$, and α is the degree of dissociation which is evaluated from the conductometric ion pair dissociation constant,[9] K. Bjerrum's theory expresses K as a function[10] of a "distance of closest approach" which, for hydrochloric acid in partly aqueous media, closely approximates s.[9] Therefore, using conductometric K values[11] for solvents high in ethanol and equation 3 for the lower compositions, we have derived s values for the entire range of composition, and these values are shown in Fig. 2. Interpolation in Fig. 2 permits estimation of K, and hence of y, for the two solvents containing 50 and 75 mole % ethanol for which e.m.f. data are available. These estimates of y are probably accurate to better than 1% at concentrations below 0.01 N.[9]

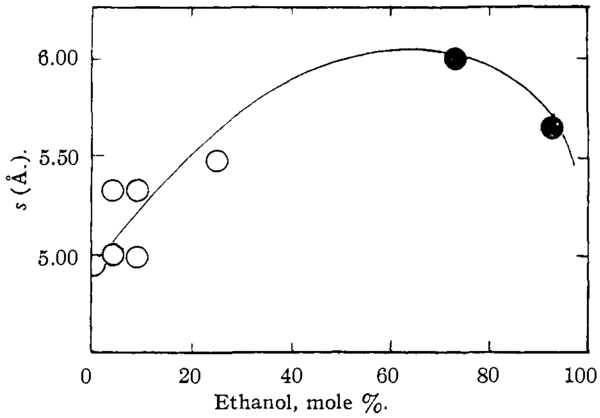

Fig. 2.—s-Values in the system ethanol–water.

The results are summarized in Table I.

(4) We have calculated the degenerate activity

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[1] (a) Based in part on the M.S. Thesis of E. F. Sieckmann, Florida State University, Tallahassee, Florida, June, 1952; (b) Physics Dept., Cornell University, Ithaca, N. Y.

[2] N. J. Anderson, Ph.D. Thesis, University of Chicago, Chicago, Ill., 1934.

[3] H. S. Harned and R. W. Ehlers, This Journal, **54**, 1350 (1932).

[4] H. S. Harned and M. E. Fleyscher, *ibid.*, **47**, 82 (1925).

[5] A. Patterson and W. A. Felsing, *ibid.*, **64**, 1478 (1942).

[6] H. S. Harned and C. Calmon, *ibid.*, **61**, 1491 (1939).

[7] J. W. Woolcock and H. Hartley, *Phil. Mag.*, [7] **5**, 1133 (1928).

[8] J. L. Hall and H. Phillips, Chemistry Department, West Virginia University; private communication from Dr. J. L. Hall.

[9] H. P. Marshall and E. Grunwald, *J. Chem. Phys.*, **21**, 2143 (1953).

[10] See, for example, H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Pub. Corp., New York, N. Y., 1943, pp. 42, 122; p. 330.

[11] Calculated from data of I. I. Bezman and F. H. Verhoek, This Journal, **67**, 1330 (1945) by the method of ref. 9.

coefficient of chloride ion, f_{Cl}, from the e.m.f. data, using the equation

$$E^0_c - E^0_c(\mathrm{HOH}) = -0.05915 \log (f_H f_{Cl}) \quad (5)$$

and available values of f_H for lyonium ion.[12] The pertinent data at various rounded solvent compositions are given in Table II, which also lists values of f_{OH} for lyate ion.[12] It is seen that the solvent dependence of f_{Cl} closely resembles that of f_{OH}, but departs grossly from that of f_H. The results corroborate the view, based on entirely different evidence,[13] that solvation energies of anions in hydroxylic media are much less sensitive to solvent change than those of cations.

TABLE I

DATA FOR CELL 1 IN THE SYSTEM ETHANOL-WATER AT 25.0°

Ethanol, mole %	D^a	s (Å.)	$K(M)$	E^0_c (mv.)	Ref.
0.00	78.48	4.95[b]	Large	221.5	10
4.17	72.99	5.00	Large	214.9	5
		5.32		215.4	6
8.91	67.54	5.32	Large	207.0	5
		4.95		209.1	6
25.00	51.35	5.45	Large	184.6	4
50.00	36.60	5.93	0.176	143.3	4[c]
72.75	29.68	5.99	.0546	....	11
75.00	29.18	5.98	.0502	87.4	4
92.27	25.77	5.65	.0251	....	11
100.00	24.306	3.60	.00915	−88.6	9

[a] Reference 8. [b] G. J. Hill and D. J. G. Ives, *J. Chem. Soc.*, 318 (1951). [c] This research.

TABLE II

VALUES OF f_{Cl}

Ethanol, wt. %	E^0_c	log f_H[a]	log f_{Cl}	log f_{OH}[a]
0.0	221.5	0.000	0.000	0.00
20.0	208.0	.008	.220	.32
35.0	195.8	.042	.392	.53
50.0	180.0	.251	.451	.63
65.0	157.9	.542	.533	.75
80.0	119.2	1.152	.577	.76
100.0	−88.6	4.707	.536	.8

[a] Reference 12.

The authors are indebted to the Research Corporation and to the Florida State University Research Council for financial support, and to Drs. J. L. Hall and H. Phillips for permission to quote their dielectric constant data.

[12] B. Gutbezahl and E. Grunwald, THIS JOURNAL, **75**, 565 (1953).

[13] P. M. Gross, *Chem. Revs.*, **13**, 99 (1933).

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Tertiary Butyl Hypochlorite as an N-Chlorinating Agent

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It has recently been shown that *t*-butyl hypochlorite (TBH) can be used in place of inorganic hypochlorites in the synthesis of hydrazine from either ammonia or urea.[1,2] Spectroscopic investigation of the corresponding reaction mixtures showed that the N-chloro compounds, that is, chloramine and N-chlorourea, are formed as the intermediate products. Although neither one of the N-chloro compounds was isolated in these instances it was considered highly probable that TBH might serve as an effective N-chlorinating agent. The general usefulness of TBH for this purpose has now been demonstrated by the synthesis of a number of typical N-chlorinated derivatives, examples of which are listed in Table I.

TABLE I

PREPARATION OF N-CHLORO COMPOUNDS USING *t*-BUTYL HYPOCHLORITE

Compound	Melting point (boiling point)	Yield, %
N-Chlorophthalimide	181–183	74.6
N-Chlorosuccinimide	150–151	35.2
N-Chloro-*o*-toluenesulfonamide (Na salt·2H$_2$O)	~170 dec.	83.9
N-Chloroacetanilide	91[a,b]	22.7
N-Dichloro-*t*-octylamine	98.5–100.5 at 18 mm.	74.8
N-Dichloro-*t*-butylamine	~30 at 16 mm.	60.5

[a] The larger part of the product mixture was converted into 4-chloroacetanilide, m.p. 173–174°; rearrangement takes place readily upon the addition of acetic acid. If the reaction is carried out in acetic acid as the solvent, only the 4-chloroacetanilide is obtained. [b] A parallel experiment with sodium hypochlorite as the chlorinating agent gave a 33.2% yield of 4-chloroacetanilide.

t-Butyl hypochlorite also may be used to prepare N-dichloro derivatives. This was accomplished specifically in the synthesis of two previously unknown N-dichloro-*t*-alkylamines. In effecting the N-chlorination of *t*-octylamine, an amount of *t*-butyl alcohol corresponding to that required by the following equation was recovered by distillation from the reaction mixture

$$\mathrm{RNH_2 + 2ROCl \longrightarrow RNCl_2 + 2ROH}$$

In effecting the synthesis of N-chlorosuccinimide by the action of TBH upon succinimide a more extensive investigation was carried out to determine the influence of such variables as temperature, solvent and time. Results are summarized in Table II.

TABLE II

PREPARATION OF N-CHLOROSUCCINIMIDE

Expt. no.	Reaction time, hr.	Temp., °C.	Mole ratio TBH: succinimide	Solvent	Yield, %
A	1	0	1:1	Acetic acid, saturated with sodium acetate	Trace
B	1	0	1:1	$HC_2H_3O_2$	14.8
C	6.5	0	2:1	$HC_2H_3O_2$	34
D	1	0	1:1	50% $HC_2H_3O_2$ in H_2O	31.3[a]
E	1	25	1:1	50% $HC_2H_3O_2$ in H_2O	36.5
F	1	0	1:1	Tetrahydrofuran	None

[a] In carrying out a comparable experiment using aqueous sodium hypochlorite in place of TBH a 35.2% yield of the desired product was obtained.

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[1] L. F. Audrieth, E. Colton and M. M. Jones, THIS JOURNAL, **76**, 1428 (1954).

[2] E. Colton, M. M. Jones and L. F. Audrieth, *ibid.*, **76**, 2572 (1954).