The writers wish to express their indebtedness to Professor D. P. Smith for his kindness in discussing these results.

Summary

Freezing point measurements have been made in order to investigate the possibility of intermolecular compound formation in solutions of ethylene chloride in benzene and in ether. The equilibrium diagrams which have been constructed for the two systems give no sign of compound formation in the ethylene chloride–benzene system, but indicate the formation of an unstable compound $C_2H_4Cl_2 \cdot 3(C_2H_5)_2O$.

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[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

The Normal Potential of the Silver–Silver Iodide Electrode from 5 to 40°

BY BENTON BROOKS OWEN

The discordance between the recorded values of the normal potential of the silver–silver iodide electrode appears to be due to incomplete knowledge of the activity coefficient of hydriodic acid and the instability of its solutions, rather than to some uncertainty in the thermodynamic behavior of silver iodide. Various investigators[1] attest the stability and reproducibility of the electrode itself, and the general trustworthiness of measurements made with it in neutral solutions[1a,b] has recently been established[2] by the isopiestic method of comparing the activity coefficients of potassium chloride and iodide. Preliminary measurements[3] indicated that these electrodes behave normally in alkaline buffer solutions also. In the present research the normal potentials of two convenient types have been determined by comparing the silver iodide and silver chloride electrodes in borax solutions containing the corresponding halide. The method should be applicable to the study of other electrodes for which the determination of normal potentials by direct extrapolation is impracticable.

Discussion of the Method

The cells employed are of the type

$$H_2 \mid HBO_2(m_1),\ NaBO_2(m_2),\ KX(m) \mid AgX,\ Ag$$

in which X represents either iodide or chloride. The required normal potential can be conveniently expressed in terms of the potential of the cell (E_{KX}), the buffer ratio ($\rho = m_{HBO_2}/m_{BO_2^-}$), and the ionization constant (K) of boric acid[4] by the equation

$$E^0_{HX} - f(\gamma) = E_{KX} + k \log m + k \log \rho + k \log K \quad (1)$$

in which $f(\gamma)$ has been written for $k \log (\gamma_{Cl^-}\gamma_{HBO_2}/\gamma_{BO_2^-})$, and k for $0.00019844\ T$. Since $f(\gamma)$ vanishes for $\mu = 0$, E^0_{HX} can be determined by extrapolation of measurements on solutions obtained by successive dilutions of a suitable stock solution. This procedure was used to evaluate E^0_{HI} at 25°,[3] but was subsequently abandoned in favor of a less laborious method based upon the experimental fact[5] that $f(\gamma)$ is only 0.01 m. v. in borate buffers when $\rho \approx 1$, and $\mu \approx 0.01$. Furthermore, $f(\gamma)$ is practically uninfluenced by the substitution of similar ions (Na^+ for K^+) at the concentrations studied.[5] Accordingly, by writing equation (1) for both KI and KCl we obtain

$$E^0_{HI} = E^0_{HCl} + E_{KI} - E_{KCl} + k \log \frac{m_{KI}}{m_{KCl}} + k \log \frac{\rho_{KI}}{\rho_{KCl}} \quad (2)$$

Upon imposing the additional experimental condition that $m_1 = m_2 \approx m \approx 0.005$ in both solutions,[6] the last term may be neglected. In practice it is convenient to make up solutions approximating the above condition, and to adjust the observed potentials to correspond exactly to $m_1 = m_2 = m = 0.005$ by the equation

$$E^{0.005}_{KX} = E_{KX} + k \log (m_{KX}/0.005) \quad (3)$$

Equation (2) may therefore be written

$$E^0_{HI} = E^0_{HCl} + E^{0.005}_{KI} - E^{0.005}_{KCl} \quad (4)$$

Materials and Technique

The purification of the borax and potassium chloride, the preparation and manipulation of solutions, and the preparation of the hydrogen and silver–silver chloride electrodes are described

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(1) (a) Gelbach, THIS JOURNAL, **55**, 4857 (1933); (b) Harned and Douglas, *ibid.*, **48**, 3095 (1926); (c) Pearce and Fortsch, *ibid.*, **45**, 2852 (1923); (d) Gerke, *ibid.*, **44**, 1684 (1922); (e) Noyes and Freed, *ibid.*, **42**, 476 (1920); (f) Taylor, *ibid.*, **38**, 2295 (1916); (g) Jones and Hartmann, *ibid.*, **37**, 752 (1915).

(2) Robinson, *ibid.*, **57**, 1161 (1935).

(3) Owen, *ibid.*, **56**, 2785 (1934).

(4) Owen, *ibid.*, **56**, 1695 (1934).

(5) *Cf.* uppermost curve in Fig. 1, Reference 4.

(6) Departures from this condition of ±10% would introduce an error of only 0.01 to 0.02 m.v.

elsewhere.[4] Baker and Adamson "analyzed" potassium iodide was brought to exact neutrality and twice recrystallized from water below[7] 60°. It was dried in a vacuum desiccator for three days, and finally heated for twenty-four hours at 50° in the air. Concentrations were calculated from the weights of "dry" salts.

The silver iodide electrodes were prepared by two different methods. According to the first method, silver iodide was produced by the electrolysis of spongy silver derived from the decomposition of silver oxide paste[7] at 450°. The weight of silver was about 0.75 g. per electrode, and electrolysis proceeded for two hours at 1 to 1.5 ma. Mixing of the anode and cathode portions during electrolysis was prevented. Electrodes prepared in this manner were always kept in cell solution until used (usually overnight). They were carefully protected from daylight, but were momentarily exposed to diffuse red light[8] from a 25-watt photographic "dark room" bulb while being inserted into black, light-proof cells. Later experiments indicated that protection from short exposure to diffuse daylight, or from direct illumination by the red bulb was not essential.

The second method of preparation involved a fusion[1e] of the silver iodide, since the electrodes were formed by the thermal decomposition of a mixture of silver iodate (1 part) and silver oxide (9 parts) heated to 650° for seven or eight minutes.[9] Contrary to expectations, a co-precipitated mixture of the oxide and iodide seemed less reliable than the mixture just described, but a co-precipitated mixture of oxide and iodate was satisfactory. No precautions were taken to protect these electrodes from diffuse daylight, either during preparation or in use.[10] They were usually kept dry until used, but a number were allowed to stand in cell solution overnight to hasten equilibrium and avoid the risk of introducing air into the cells. The latter treatment resulted in slightly more concordant readings among duplicate cells, but hardly justified the additional manipulation.

Discussion of the Results

The final experimental results calculated by equation (3) are given in Table I.

TABLE I

OBSERVED VALUES OF $E_{\mathrm{KX}}^{0.005}$

$t°$	Electrolytic AgCl (a)	(b)	Electrolytic AgI (c)	(d)	Fused AgI (e)	(f)
5	0.88181	0.88180	0.50080	0.50072	0.50074	0.50083
10	.88745	.88746	.50809	.50810	.50807	.50814
15	.89312	.89313	.51540	.51544	.51538	.51545
20	.89890	.89895	.52282	.52277	.52271	.52280
25	.90475	.90477	.53021	.53013	.53005	.53010
30	.91049	.91046	.53752	.53743	.53740	.53739
35	.91624	.91622	.54484	.54476	.54473	.54473
40	,92196	.92202	.55222	.55210	.55208	.55206
$m \times 10^6$	4832	4821	5031	4912	5309	4834

Two independent stock solutions were devoted to the study of each type of electrode, and twelve similar cells were filled with each solution—six for temperatures from 5 to 25°, and six from 20 (25) to 40°. The mean deviation of individual cells from the recorded averages is about 0.05 mv. All six (twelve, at over-lapping temperatures) cells are included in the average unless, as occasionally happened, a cell showed departures exceeding 0.15 mv. The difference between the results obtained with fused and electrolytic silver iodide is no greater than that observed between duplicate series with either type. Therefore series (c), (d), (e), and (f) were averaged to obtain final values of $E_{\mathrm{KI}}^{0.005}$, and (a) and (b) were averaged to obtain final values of $E_{\mathrm{KCl}}^{0.005}$. These values were combined, according to equation (4), with the smoothed values of E_{HCl}^{0} given by Harned and Ehlers,[11] and the results recorded in Table II as E_{HI}^{0}. E_{AgI}^{0} is, of course, equal to $-E_{\mathrm{HI}}^{0}$. The temperature variation of E_{HI}^{0} is satisfactorily represented by the equation

$$E_{\mathrm{HI}}^{0} = -0.15219 - 328 \times 10^{-6}(t - 25) - 3.6 \times 10^{-6}(t - 25)^2 \quad (5)$$

TABLE II

E_{HI}^{0} FOR THE CELL H_2 | HI | AgI, Ag AND THE DISSOCIATION CONSTANT OF BORIC ACID

$t°$	E_{HI}^{0}	Eq. (5)	pK	Eq. (6)
5	−0.14712	−0.14707	9.440	(9.434)
10	− .14805	− .14808	9.380	9.379
15	− .14920	− .14927	9.326	9.328
20	− .15062	− .15064	9.279	9.280
25	− .15225	− .15219	9.237	0.237
30	− .15396	− .15392	9.198	9.197
35	− .15586	− .15583	9.164	9.162
40	− .15787	− .15792	9.132	9.131

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(7) Jones and Hartmann, THIS JOURNAL, **37**, 241 (1915).

(8) Although photographic (bromide) film is sensitized to red light by a trace of silver iodide [Renwick, *Phot. J.*, **61**, 12 (1921); *Brit. J. Phot.*, **67**, 743 (1920)], pure silver iodide is relatively insensitive to red light unless it has been previously exposed to intense illumination by violet (or white) light [Scholl, *Ann. Physik.*, [4] **16**, 193, 417 (1905)].

(9) *Cf.* Harned and Keston, THIS JOURNAL, **57**, 1671 (1935).

(10) Although the cells were not blackened in this case, considerable light protection was afforded by clamps, and the walls of the thermostat.

(11) Harned and Ehlers, THIS JOURNAL, **55**, 2179 (1933). The values of E_{HCl}^{0} selected were calculated by equation (7) of their paper.

Table II also includes values of pK for boric acid calculated from the average $E_{\mathrm{KCl}}^{0.005}$ by equation (1). Their agreement with results previously reported[4] in the form

$$pK = 9.023 + 8 \times 10^{-5} (76.7 - t)^2 \qquad (6)$$

is within the estimated error of ±0.002, except at 5° where experimental results were not obtained in the earlier work. Incidentally, this concordance is sufficient justification for neglecting $f(\gamma)$ in the derivation of equation (4).

On the basis of the average deviation of duplicate cells in the same, and in different series (Table I), the final average values of $E_{\mathrm{KX}}^{0.005}$ are apparently reproducible to about ±0.05 mv. A difference of ±0.03° in the calibration of the thermometers used in this research and in the determination of E_{HCl}^0[11] would be equivalent to ±0.05 mv. also, and an equal uncertainty may be attributed to E_{HCl}^0. Accordingly, the recorded values of E_{HI}^0 can reasonably be considered *reproducible* to better than ±0.2 mv. The question of absolute accuracy is much more difficult to deal with, since it depends upon the purity of the electrode reaction in the presence of borax, as well as the absolute accuracy of E_{HCl}^0. Noyes and Freed[1e] reported -0.1477 at 25°, and the value, -0.151, given in the "International Critical Tables" (VI, p. 332), is based upon the data of Pearce and Fortsch[1c] at the same temperature. Both of these figures were arrived at, of course, by the use of certain assumptions regarding the behavior of the activity coefficient of hydrogen iodide at, and below, the concentrations studied. If it be assumed that more "reasonable" values for the activity coefficient would be given by $\gamma_{\mathrm{HI}}/\gamma_{\mathrm{HBr}} = \gamma_{\mathrm{HBr}}/\gamma_{\mathrm{HCl}}$, then the corresponding E_{HI}^0, arranged in order of decreasing concentrations, would be -0.1527 and -0.1509 (N. and F.); -0.1525, -0.1522, -0.1525, -0.1523, -0.1507, -0.1512, and -0.1512 (P. and F.). Although this recalculation on a common, arbitrary basis demonstrates the essential compatibility[12] of the previous investigations, it cannot be used to establish the *absolute* value of E_{HI}^0. It strongly suggests, however, that this value should lie within the limits -0.151 and -0.153. A more forthright and rigorous check upon the figures in Table II would require sufficiently extensive and consistent measurements in dilute hydriodic acid to permit an unambiguous extrapolation.

Summary

1. A method is described by which the normal potentials of certain electrodes may be compared in borax solutions without recourse to extrapolation.

2. The normal potential of the silver–silver iodide electrode has been determined from 5 to 40°. Results obtained with electrolytic and with fused silver iodide are practically indistinguishable.

3. The dissociation constant of boric acid has been calculated from new measurements at μ = 0.01 molal. The results agree with previously reported values obtained by extrapolation.

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[12] Values of E_{HI}^0 evaluated by combining various cells with liquid junctions, equilibrium data, etc., differed among themselves by as much as 16 m.v. in extreme cases, but by using recent values for the calomel electrodes ("Int. Crit. Tables," VI, p. 332) results ranging between -0.150 and -0.151 were obtained from the data of Hass and Jellinek [*Z. physik Chem.*, **A162**, 153 (1932)], Goodwin [*ibid.*, **13**, 645 (1894)], and Jones and Kaplan [THIS JOURNAL, **50**, 1845, 2066 (1928)].