GLASS ELECTRODE POTENTIOMETRY IN GLACIAL ACETIC ACID

Andrew Teh-an Cheng

Roed A. Howald[1] and

David L. Miller[2]

One important aspect of the behavior of ion pairs in solvents of low dielectric constant is the influence of polar molecules and other ion pairs on the thermodynamic activity of the ion pairs. Dipole-dipole forces should be quite strong in such cases, and fairly large "salt effects" may be expected. These equilibrium salt effects may provide insight into the kinetic salt effects observed for certain reactions in the same solvent. This work is primarily an investigation of the suitability of the glass, chloranil, and silver-silver chloride electrodes for such measurements in glacial acetic acid.

There are a large number of experimental observations which indicate the sensitivity of glass electrodes to water. A glass electrode which has not been soaked in water for a long time must be restandardized frequently when used in dilute aqueous solutions. Measurements in concentrated aqueous solutions have led to the suggestion[2] that the glass electrode responds to the activity of H_3O^+ rather than H^+. This cannot be completely correct, since in that case measurements under nearly anhydrous conditions would be erratic and quite unreliable, in sharp contrast to the results obtained in acetic acid in a number of laboratories[3-5] including the general use of the glass electrode for potentiometric acid-base titrations in glacial acetic acid[5,6]. Some measure of the accuracy with which the glass electrode provides a direct measure of the hydrogen ion activity is available from direct comparison with the hydrogen electrode over the range 0 to 96% acetic acid in water[3] and from an indirect comparison with the quinhydrone electrode[4]. These studies indicate that glass electrode potentials are reliable thermodynamically to within 15 and 5 millivolts respectively.

This general level of reliability for the glass electrode has been confirmed in this work by repeated measrements over a period of months on the same solution and by direct comparison with the chloranil electrode. Readings in error by as much as 30 millivolts were observed following drastic changes in the water concentration, however even without special care or prolonged standing before readings there was agreement within 20 mv. between the glass and chloranil electrodes during the course of acid base

(1) Address inquiries to Dr. R. A. Howald, Chemistry Department, St. John's University, Jamaica 32, L. I., N. Y. U. S. A.

(2) Address inquires to Mr. David L. Millor, Chem. Dept. Harvard Uuiversity, Cambridge 38, Mass. U. S. A.

titrations. Thus thermodynamic data, equilibrium constants and activity coefficients, can be readily obtained with a glass electrode in acetic acid with an uncertainty of less than a factor of 2 even in exceptionally unfavorable cases. In particular, data on the effect of water on acid base titrations in acetic acid are reported here, complementing and extending the recent studies of Bruckenstein and Kolthoff[9] and Schwartzenbach and Stensby[10]. Correlations are also possible between this potentiometric data on activities and studies of vapor presure and freezing point depression.

Experimental

To avoid the uncertainty involved with liquid junction potentials all the electrodes used were placed in the same flask. A 100 ml. flask was fitted with four long necks as in Fig 4. The central vertical neck was fitted with a mechanical stirrer operating through a loose fitting cork. A glass electrode, Beckman 1190-80, or 40498, and Ag/AgCl electrode, Beckman 1264 or 39261, were each sealed with picein cement into one of the necks. The fourth neck was used for the introduction of a long capillary buret tip as well as for platinum electrodes and hydrogen when they were used. This neck was loosely stoppered with a suitably bored cork. The two necks which were not tightly sealed were about 20 cm. long, sufficient so that the pickup of moisture from the air by the solution in the flask was negligible. The flask was immersed in a water bath adjusted to 25°C. A second similar flask was constructed from a 50 ml. flask and fitted with a second pair of electrodes.

An ordinary run consisted of a series of about 25 potential readings taken over a period of several hours as portions of a sodium acetate solution were added from the buret to an initially acid solution. The potential measurements were made with a Beckmann model G pH-voltmeter. When three electrodes were used, measurements were made comparing both of the other electrodes to the glass electrode. In a few cases the other electrodes were compared directly, giving a reading negligibly different from the difference of the other two values. In other runs portions of water or a solution of water in acetic acid were added to HCl or sodium acetate solutions.

Solutions of HCl in acetic acid were prepared by adding concentrated aqueous hydrochloric acid and acetic anhydride to glacial acetic acid. These solutions lost HCl on standing and when they were poured into the flask containing the electrodes. On standing in this flask there were additional smaller losses of HCl shown by a drift in the potential readings. The concentrations of HCl present were calculated from the amount of sodium acetate solution required to reach the equivalence point of the titration as determined from a plot of potential vs. volume of sodium acetate solution added. All other concentrations were calculated from the initial concentrations of the solutions used assuming negligible volume changes on mixing. The water content of each original solution was determined by Karl Fischer titration. In a number of the runs the water content of the final solution was also determined. This was generally somewhat higher than the value calculated from the water contents of the component

solutions, corresponding to the pickup of one to three extra milliequivalents of water in the process of filling the cell. In calculating the water concentrations it was assumed that this extra water was present at the beginning of the series of measurements.

Standard C. P. and reagent grade chemicals were used throughout. The glacial acetic acid used generally contained 0.05 to 0.10 M water. Sodium acetate solutions were prepared from anhydrous material or from the trihydrate, adding acetic anhydride and refluxing for at least 10 hours when lower water concentrations were desired. These solutions were standardized by potentiometric titration vs. a solution of $HClO_4$ in glacial acetic acid using $Na_2CO_3.H_2O$ as a primary standard. A 0.643 M sodium perchlorate solution was prepared by weighing the anhydrous salt which was obtained by storing the monohydrate on a watchglass in a dessicator over drierite for 7 weeks. Portions of glacial acetic acid and sodium perchlorate were dried further by refluxing with acetic anhydride, but in most of the work no attempt was made to operate with water concentrations of less than 0.1 M.

Between some of the runs the electrodes were checked by obtaining potential readings for a standard reference solution. Three such solutions were used; all moist sodium acetate solutions saturated with NaCl.

The initial solution was saturated with NaCl before some of the titrations. For this purpose finely divided NaCl was prepared by the addition of HCl to a solution of sodium acetate in acetic acid. The precipitated NaCl was collected and washed with methanol. Distillation Products Industries, tetrachlorohydroquinone (white label) and chloranil (practical) were recrystallized from acetic acid before use.

Calibration of the Glass Electrode. Electrode Drift

The glass electrode responded rapidly to changes in the acidity of the acetic acid solutions. On taking alternate readings on solutions of HCl and sodium acetate saturated with NaCl, after each change the readings were nearly constant after three minutes. Nevertheless slow drift of the potential readings was observed under certain conditions, depending on the nature of the solution and the past history of the electrodes. The first reference solution was used with the glass - Ag/AgCl electrode pair over a period of almost 4 months. About 90% of the potential readings with this combination at 25°C were within the range 352±4 millivolts, but values as high as 379 mv. were obtained immediately following measurements on solutions with H_2O concentrations of around 8 M. This reference solution was itself approximately 1.4 M in H_2O. In these cases the readings dropped on prolonged standing with the reference solution, but as much as 24 hours was sometimes inquired for apparently complete recovery. An attempt was made to get larger transient effects by changing from an aqueous solution to a reference solution 0.43 M in H_2O, but the drift following this change was less than 10 mv. Repeated measurements on a reference solution can also show long term changes in the glass electrode. Such an effect is shown in the measurements with the second glass electrode; they show a slow increase of 25 mv. over the first month of use.

Another source of data on the reliability of the glass electrode in this work is the reproducibility of readings on similar solutions. The agreement in relative potentials in the course of repeated titrations is generally excellent, within 5 mv, provided the water concentration is 0.2 M or higher. To attain this level of reproducibility it is necessary to ground the pH meter and the water bath and to allow sufficient time for equilibrium to be established in the solubility of sodium chloride. The first points beyond the equivalence point in a titration of HCl with sodium acetate are often high due to supersaturation with sodium chloride. The precipitation of NaCl from a dry acetic acid solution is quite slow even with plenty of seed crystals available. As much as 20 minutes with vigorous stirring may be required to establish equilibrium with 0.3 M H_2O present. Equilibrium is reached faster at higher water concentrations, but the addition of water also decreases the sharpness of the end point. as described below.

An attempt was made to calibrate the glass electrode by direct measurement versus a hydrogen electrode. The hydrogen electrode has been used sucessfully in glacial acetic acid[9-10,3], however these publications indicate that extreme precautions are necessary to obtain reliable potentials in dry solutions. A number of glass vs. hydrogen electrode readings were obtained in the range 680 to 695 mv. using one of the wet reference solutions. This is a reasonable range for variation in the glass electrode in the light of the other data. However with the electrodes and apparatus for hydrogen purification which we used it was impossible to obtain reproducible potentials with the hydrogen electrode in dryer HCl solutions. The observed potentials versus the glass electrode ranged from 385 to 677 mv.

In view of these difficulties with the hydrogen electrode, the glass electrodes were calibrated by comparison with the chloranil electrode. Since both chloranil, $C_6Cl_4O_2$, and tetrachlorohydroquinone, $C_6Cl_4O_2H_2$, are only moderately soluble in acetic acid, it is quite simple to keep the solution saturated and their activities constant. Thus the chloranil electrode is sensitive only to the activity of hydrogen ions. As long as the solid phases are the acetic acid solvates, the potential of a chloranil electrode versus a hydrogen electrode should be 680 mv., the E° value reported by Heston and Hall[11]. The chloranil electrode is susceptible to poisoning, but much less so than the hydrogen electrode. Twice in the course of this work the glass vs. chloranil readings suddenly increased by about 500 mv., but the original reading was restored by replacing the platinum electrode. The principal disadvantage of the chloranil electrode is the sensitivity of the Ag/AgCl electrode to the presence of chloranil and tetrachlorohydroquinone. The presence of these materials introduced an error in the Ag/AgCl potentials of from 0 to 80 millivolts depending on the solution and the condition of the Ag/AgCl electrode. Thus while the chloranil electrode could be used to check the glass electrode in a particular type of titration, any quantitative conclusions must be based on similar titrations with chloranil absent.

As expected from the drift effects described above for the glass elecsrode, the glass vs. chloranil electrode measurements were not entirely reproducible. Readings with the

first glass electrode in solutions which had been stirred with chloranil and tetrachlorohydroquinone in the presence of the electrodes for an hour or more fell into two groups, -10 ± 2 and -28 ± 6 mv. The lower values were mostly obtained following measurements at exceptionally high water concentrations. A somewhat larger range was observed during titrations: -25 to 0 mv. for titrations of HCl with sodium acetate and -40 to 11 mv. for runs in which successive portions of water were added to solutions of HCl in acetic acid. The range -10 ± 15 mv. includes essentially all the experimental values for the difference between the first glasselectrode and the chloranil electrode obtained when the water concentration was consistently maintained below 2 M.

The second glass electrode gave higher readings. These values increased still more during the first month while the readings on the reference solution rose. The difference between these two types of measurements was nearly constant at about 323 mv. Because of this steady drift, the changes in potential during the various types of titration are more significant than the actual values. The spread between the highest and lowest values in particular titration were: HCl vs. sodium acetate, 4, 9, and 20 mv.; HCl vs. H_2O, 12, 17, and 23 mv.; and sodium acetate vs. H_2O, 8, 11, and 12 mv.

Combining the glass vs. chloranil potential measurements with the E° value for the chloranil electrode in glacial acetic acid[13] gives 670 ± 15 mv. for the standard potential of the first glass electrode. This is in excellent agreement with the best of the direct measrements against the hydrogen electrode cited above. The corresponding values for the sencond glass electrode ranged from about 720 to 760 mv.

An additional calculation of E° for the glass electrodes used here is possible from the measurements of glass vs. Ag/AgCl potentials at known concentrations of HCl and H_2O. The reading of a hydrogen electrode vs. the Ag/AgCl electrode in such a solution can be calculated from the data of Aston and Gittler[14] for the potential of this electrode pair as a function of the HCl partial pressure in atmospheres, $E=150.8-59.1$ log pH Cl. The potential for a given HCl concentration can be calculated using the Henry's law constant, 0.334 atm. l. $mole^{-1}$, measured by Rodebush and Ewart[13]. Then a correction can be made for the effect of the H_2O on the activity of HCl from the measurements described below. The E° values calculated in this way generally fall within the ranges given above, and have the advantage of giving a value determined during the particular titration under consideration. For quantitative comparisons of different runs most of the potentials given below and plotted in the figures have been corrected to values for a hypothetical glass electrode with an E° of 700 mv., correcting all potentials in a run on the basis of one point during the run or a measurement on one of the reference solutions immediately preceding or following the run.

Solutions of HCl. The Effect of Water.

The dependence of the glass vs. Ag/AgCl potentials on the concentration of HCl was given within experimental error by the equation $E=Z+59.1$ log C_{HCl}. Thus Henry's law is followed within experimental error by solutions of HCl in acetic acid over the

concentration range from 0.003 to 0.18 M, and ionization and association of the HCl must both be small. This agrees well with the direct experimental test of Henry's law[13], and with the generally low values (ca. 10^{-7}) found for ionization constants in acetic acid generally[14]. Moreover HCl is a weak acid in glacial acetic acid with an ionization constant even smaller than 10^{-7} [15]. The potentiometric data of Mukherjee[16] on HCl solutions in acetic acid is inconsistent with these considerations and with the data reported here, apparently because of the failure of his hydrogen electrode to give reliable potentials in this solvent.

The addition of water lowers the activity of HCl and the observed potentials. Thus the quantity "Z" from the above equation, the potential corrected for the HCl concentration, is a funtion of the water concentration of the solution as well as the standard electrode potential of the particular glass electrode being used. Comparable values can be obtained by correcting the potentials to an E° values of 700 mv. for the glass electrode. These corrected "Z" values from a number of different runs are plotted against the water concentration in figure 1. The irreproducibility of the values at the lowest water concentrations is evident. However the agreement in most runs over the concentration range from 0.3 to 6 M H_2O is excellent. This data cannot be fitted by the formation of a single complex species such as H_3OCl, and there is no appreciable linear region with any integral slope in a plot of Zcorr. vs. log C_{H_2O}. Thus it appears best to treat the effect of water as a medium effect.

For the data obtained in solutions saturated with NaCl shown in figure 1, there is excellent agreement with the equation $E_{corr.} = 823 - 33.1\, C_{H_2O} + 1.77\, C^2_{H_2O}$ shown as a solid line in the figure. Thus the potentials corrected to E°=700 are given by the equation

$$E_{corr.} = 823 + 59.1 \log C_{HCl} - 33.1\, C_{H_2O} + 1.77\, C^2_{H_2O}$$

Since $E_{corr}=823+59.1 \log a_{HCl}$ if one chooses a hypothetical ideal undissociated unit concentration solution of HCl in dry acetic acid as the standard state for its activity, one obtains the equation $\log \gamma_{HCl} = -0.56\, C_{H_2O}+0.03\, C^2_{H_2O}$ for the activity coefficient of HCl in these solutions.

At the higher water concentrations the solubility of NaCl is high enough to have an appreciable effects on the potentials. The data on HCl solutions with no sodium chloride present are adequately represented by the equation

$$Z_{corr} = 823 - 33.1\, C_{H_2O} + 1.18\, C^2_{H_2O}.$$

Sodium Acetate Solutions. The Effect of Water.

After excess sodium acetate has been added in a titration the electrodes still respond to the activity of HCl. However the concentration of HCl it no longer directly measureable, and its activity is determined by the equilibrium

HCl + NaOAc = NaCl(s) + HOAc.

The activity of NaCl thus has a very great influence on the readings, and failure to achieve solubility equilibrium can introduce considerable error in the observed

potentials. Thus the somewhat increased experimental scatter shown by these results in basic solutions is not unexpected. When solubility equilibrium is established, the potential should be given by the equation

$$Ecorr = 823 + 59.1 \log [K\ a_{HOAc}/a_{NaOAc}].$$

Since the activity of sodium acetate is at least approximately proportional to its concentration, with the proportionality constant γ NaOAc' this can be rearranged to give

$$Z^* corr = Ecorr + 59.1 \log C_{NaOAc} = 823 + 59.1 \log K + 59.1 \log [a_{HOAc}/\gamma_{NaOAc}].$$

Z^* may be some what dependent on the sodium acetate concentration, but such effects over the concentration range 0.005 to 0.09 M are not clearly larger than the experimental uncertainty of about 10 mv. In dilute solutions with water concentrations above 3 M, the disproportionation of NaCl to give HCl and NaOAc becomes appreciable. However ionization of the sodium acetate does not appear to be an important factor below 10 M H_2O. This can be substantiated from conductance data which yield an ionization constant of 2×10^{-7} for sodium acetate in dry acetic acid[16], and indicate that it is only about 20 times more ionized in the presence of 15 M H_2O[15]. Also the presence of NaCl should repress the ionization of sodium acetate.

The addition of water raises the potential readings in these basic solutions, with the further addition of water giving a rather flat maximum. Z^* values from a number of runs including some in which either or both the H_2O and sodium acetate concentrations were varied are shown in figure 2. Again the experimental scatter is worst for the dryest solutions. Most of the data could be fitted within 10 mv. by a straight line, however most runs show some curvature and the quadratric

$$Z^* corr = 345 + 10.6\ C_{H_2O} - 0.6\ C^2_{H_2O}$$

gives a somewhat better fit as shown in figure 2. This gives the equation

$$\log [\gamma\ NaOAc\ /a_{HOAc}] = -0.18\ C_{H_2O} + 0.01\ C^2_{H_2O}$$

for the effect of water on the activity of sodium acetate.

The Titration of HCl with Sodium Acetate.

The equations for Z and Z^* given above summarize the behavier of the potential through the course of a titration. The difference between the constant terms gives a value of 1.2×10^8 for the equilibrium constant K. The addition of water shifts the equilibrium markedly toward the left, and reduces the sharpness of the potential change at the equivalence point. The concentration equilibrium constant $1/C_{HCl}C_{NaOAc}$, is given by the equation

$$\log[K\ \gamma_{HCl}\ \gamma_{NaOAc}\ /a_{HOAc}] = 8.09 - 0.74\ C_{H_2O} + 0.04\ C^2_{H_2O}$$

The effect of water is large enough that the end point becomes quite indistinct above 6 M H_2O in titrations with 0.43 M sodium acetate. Since water lowers the potentials of acid solutions more than it raises those of basic solutions, the potential at the equivalence point is lowered somewhat. Several of the titrations with 0.43 M sodium acetate are shown in figure 3 to illustrate these points. Since large quantitites of water reduce the sharpness of the endpoint, and in the driest solutions the glass electrode appears to be

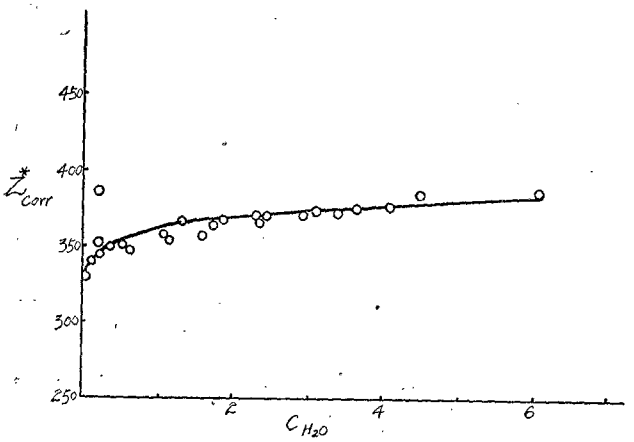

FIGURE 2
Corrected potentials in sodium acetate solutions vs. water concentration

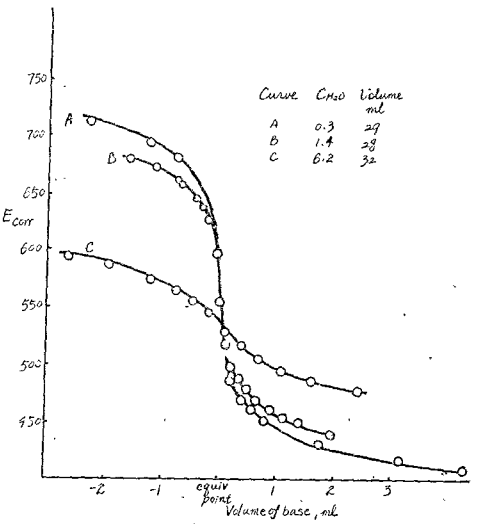

FIGURE 3
Acid Base Titration Curve
HCl titrated with 0.93M NaOAc

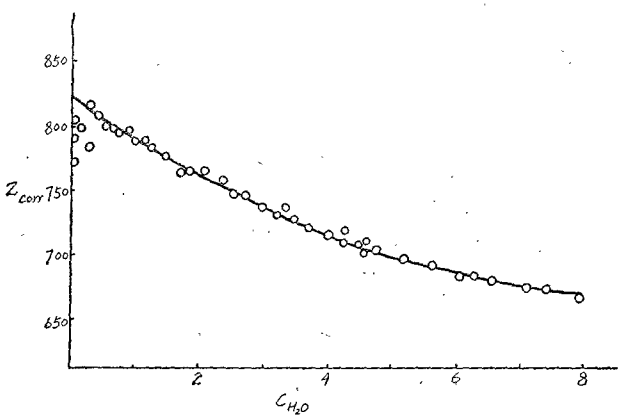

FIGURE 1
Corrected potentials in HCl solutions vs water concentration

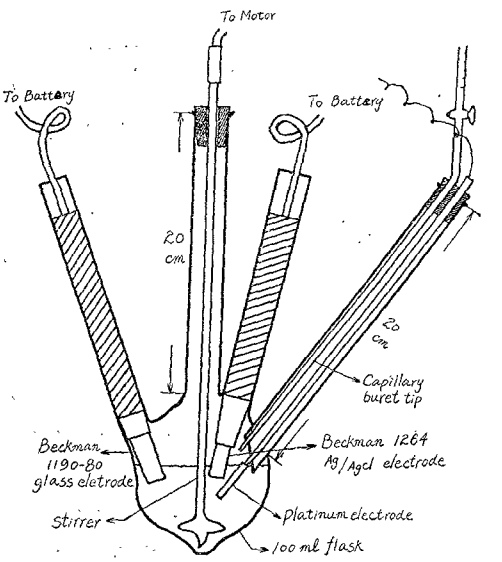

FIGURE 4
Special flask for titration

more erratic and the rates of solution and precipitation of NaCl are inconveniently slow, the best titrations from an analytical viewpoint are in the range 0.4 to 1.0 M H_2O.

Literatures cited

(1) See for example
a. R. A. Howald, *J. Am. Chem. Soc.*, to submitted
b. S. Winstein, S. Smith, and D. Darwish, *J. Am. Chem. Soc.*, ***81***, 5511 (1959)
(2) Malcolm Dole, "Glass Electrode", J. Wiley and Sons, New York (1941)
M. Dole, *J. Am. Chem. Soc.*, ***53***, 4260 (1931)
(3) J. A. Cranston andH. F. Brown, Journal of the Royal Technical College (Glasgow), ***4***, 32 (1937)
(4) N. A. Izmailov and A. M. Aleksandrova, *Zhur. Obschei Khim.*, ***20***, 2127 (1950); *J. Gen. Chem.* USSR., ***20***, 2207 (1950).
(5) T. Higuchi, M. L. Danguilan, and A. D. Cooper, *J. Phys. Chem.*, ***58***, 1167 (1954).
(6) P. C. Markunas and J. A. Riddick, *Anal. Chem.*, ***23***, 337 (1951).
(7) S. Bruckenstein and I, M. Kolthoff, *J. Am Chem. Soc.*, ***78***, 2974 (1956); ***79***, 1 (1957); ***79***, 5915 (1957).
(8) G. Schwarzenbach and P. Stensby, *Helvetica Chimica Acta*, ***42***, 2342 (1959).
(9) J. Russell and A. E. Cameron, *J. Am. Chem. Soc.*, ***58***, 774 (1936); ***60***, 1345 (1938)
(10) O. Tomicek and A Heyrovsky, *Coll. Czech. Chem. Commun.*, ***15***, 984 (1950).
(11) B. O. Heston and N. F. Hall, *J. Am. Chem. Soc.*, ***55***, 4729 (1933)
(12) J. G. Aston and F. L. Gittler, *J. Am. Chem. Soc.*, ***77***, 3173 (1955)
(13) W. H. Rodebush and R. H. Ewart, *J. Am. Chem. Soc.*, ***54***, 419 (1932)
(14) M. M. Hones and E. Griswold, *J. Am. Chem. Soc.*, ***76***, 3247 (1954)
(15) I. M. Kolthoff and A. Willman, *J. Am Chem. Soc.*, ***56***, 1007 (1934)
(16) L. M. Mukherjee, *J. Am. Chem. Soc.*, ***79***, 4040 (1957)

冰醋酸中玻璃電極之電勢測定法

本實驗旨在研究冰醋酸中玻璃電極之動態，以一連串之實驗測量其對 Ag/AgCl 電極之電勢，並直接與無液界之 Pt/Chloranil, Tetrachloro hydroquinone 等電池之電極比較，且以 20mv 之電勢在不同之狀況下觀察，若水濃度爲 0.3 M 或大於 0.3 M 時其電勢之可靠性爲 ±5mv.

含水量對鹽酸與醋酸鈉之電勢滴定法之影響亦經測定。在 10mv 範圍內，0.3M 至 6M 之含水濃度對鹽酸及以氯化鈉飽和之醋酸鈉溶液之活度影響可以下式表示之:

$$\log \gamma_{HCl} = -0.56\, C_{H_2O} + 0.03\, C^2_{H_2O} \quad \text{及}$$

$$\log [\gamma_{NaOAc} / a_{HOAc}] = -0.18\, C_{H_2O} + 0.01 C^2_{H_2O}$$