

THE BEHAVIOR OF THE GLASS ELECTRODE IN NON-AQUEOUS MEDIA

V. BEHAVIOR OF THE GLASS ELECTRODE IN GLACIAL ACETIC ACID

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This investigation is a continuation of a study of the properties of the glass electrode in non-aqueous media [1].

In the previous paper we reported a point of inflection in the calibration curve of a glass electrode of Hughes glass in the acid region. We suggested that this peculiarity in the behavior of the glass electrode would be more clearly manifested in acidic solvents. In the present investigation, therefore, we have examined the behavior of the glass electrode in acetic acid in the expectation that in this solvent deviations and inflection of the calibration curve at higher pH values would occur, coupled with the disappearance of the negative branch of the potential pH curve.

By virtue of its physical properties and its good solvent power, acetic acid is frequently used as a solvent. Hence the necessity for pH determination arises.

These pH measurements are generally carried out with the aid of the quinhydrone or chloranil electrode [2] (the chloranil electrode is an equivalent mixture of chloranil and hydrochloranil).

The chloranil electrode in acetic acid is less subject to oxidation than the quinhydrone electrode; however, its application, as well as that of the quinhydrone electrode, is attended by a number of difficulties.

The hydrogen electrode with platinum, both according to the literature [3] and our own observations, cannot be used in acetic acid. The best results are obtained by use of a gold electrode coated with palladium black [3].

Hence the use of the above-mentioned electrodes in acetic acid is limited. For this reason, as well as for the purpose of clarifying the character of the deviation of the glass electrode in acidic solvents, we have attempted to establish the practical possibility of utilization of the glass electrode in acetic acid for pH determinations.

EXPERIMENTAL

We used acetic acid from the Kharkov Reagent Factory in our investigation. Its purification by the usual method gave glacial acetic acid with $d_{4}^{17.5}$ 1.0533.

All of the measurements were performed on a potentiometric apparatus with a radio tube (a detailed account of the apparatus appears in the paper by N.A. Izmailov and I.F. Zabara [4]). We used electrodes of the Haber type constructed of electrode glass prepared according to the recipes of Hughes and MacInnes and Dole, [5].

For the purpose of calibration of the glass electrodes, a series of solutions was prepared in glacial acetic acid solution with pH values of -1.4 to +8.3. The pH scale was calibrated against an infinitely dilute solution of ions of acid in acetic acid as the standard state.

Solutions with high pH values are solutions of dimethylaniline and sodium acetate in acetic acid; solutions with low pH values are solutions of chloric acid in glacial acetic acid. Still lower pH values were obtained by preparing strongly acid solutions by the method of Russel and Cameron [3] (solutions of sulfuric and chloric acids in glacial acetic acid with addition of acetic anhydride). We added 10% acetic anhydride and not 30% as recommended by the above-mentioned authors.

The water added to the acetic acid together with the chloric acid combined with the acetic anhydride (due precautions being taken against explosion).

The compositions of the acetic acid solutions for calibration of the glass electrodes and their pH values are listed in the Table.

The pH values of the solutions in glacial acetic acid were determined with the quinhydrone electrode which was calibrated against 0.1437 molar H_2SO_4 in glacial acetic acid.

Attempts to use HCl solution as a standard were unsuccessful because a solution of as little as 0.1 N HCl in acetic acid gives off fumes.

The pH of the standard was calculated from the formula

$$pH = -\log a = -\log m\gamma^*,$$

where a is the activity, m the concentration, and γ^* the activity coefficient related to an infinitely dilute solution in acetic acid as the standard.

The value of the activity coefficient of sulfuric acid in glacial acetic acid was taken from the paper of La Mer and Eichelberger [8].

Consequently the cell for determination of pH of acetic acid solutions contained no phase boundaries, and therefore no phase potentials. The magnitude of the pH was related to an infinitely dilute solution of the ions in the same solvent. Our scale is thus a specific scale: the scale zero was a solution of acid in acetic acid with an ionic activity of unity.

The range of such a scale for acetic acid is from a pH of 0 to 11.4 (the ionic product $k_1 = 5.8 \cdot 10^{-11}$ [7]).

The glass electrodes prepared in the usual manner were first calibrated for aqueous solutions in the pH range of -0.4 to +13.85. For this purpose aqueous hydrochloric acid solutions, a series of buffer solutions according to MacIllvaine, Sørensen and Ringer, and sodium hydroxide solutions were prepared. The pH value

TABLE

No.	Composition of the solutions in glacial acetic acid	pH values
1	1-molar dimethylaniline	8.3
2	1.0 N CH_3COONa	8.1
3	0.25 N CH_3COONa	7.6
4	0.1 N CH_3COONa	7.25
5	0.01 N CH_3COONa	6.7
6	0.1 N CH_3COONa + ~ 0.1 N $HClO_4$..	6.3
7	0.05 N $HClO_4$	3.4
8	0.1 N $HClO_4$	2.1
9	0.2 N $HClO_4$	1.4
10	0.004 molar H_2SO_4 + 10% acetic anhydride	0.3
11	0.007 molar H_2SO_4 + 10% acetic anhydride	-0.2
12	0.02 N $HClO_4$ + 10% acetic anhydride	-1.4

of the aqueous solutions was determined with the hydrogen electrode.

The calibration curves of the glass electrodes of Hughes and MacInnes glass against aqueous solutions are plotted in Figure 1.

Following this, the glass electrodes were calibrated against the acetic acid solutions. Measurements were made at 18-20° in the chain:

Hg	Hg ₂ Cl ₂	Viebel's aqueous solution	Glass	Acetic acid solution under test	LiCl, 0.1 N in acetic acid	0.01 N HCl 0.09 N LiCl in acetic acid, quinhydrone	Pt
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The siphon was filled with 0.1 N solution of lithium chloride in acetic acid. After each measurement the glass electrode was rinsed out with acetic acid. The potential of the glass electrode in acetic acid was rapidly steadied (in the course of 2-5 minutes) and subsequently remained constant. The potential only creeps in strongly acid solutions. Results of calibration of glass electrodes, constructed of two different glasses, against acetic acid solutions are plotted in Figures 2 and 3.

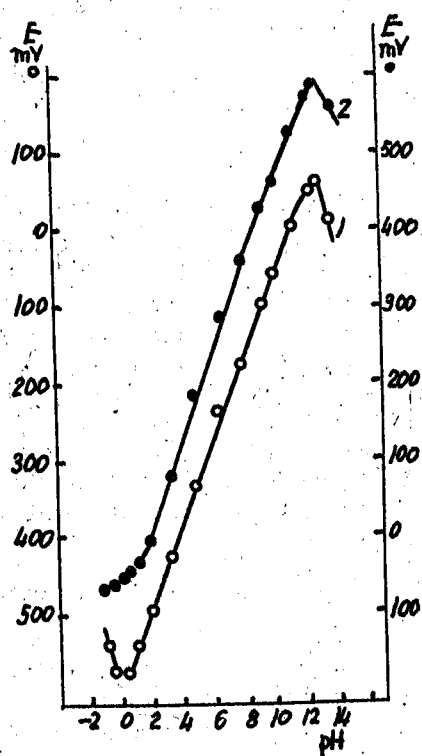


Fig. 1. Calibration curves of glass electrodes against aqueous solutions.

1-Hughes glass; 2-MacInnes and Dole Glass.

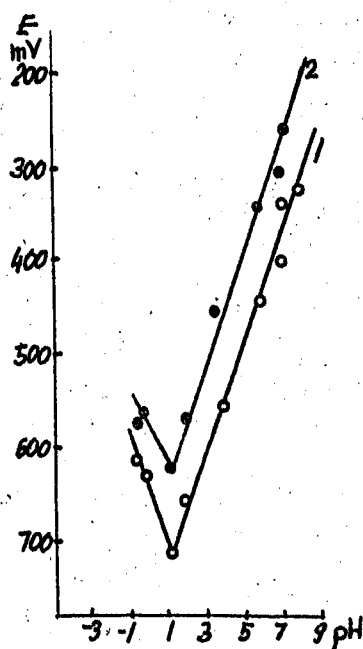


Fig. 2. Calibration curves of glass electrodes of Hughes glass against acetic acid solution.

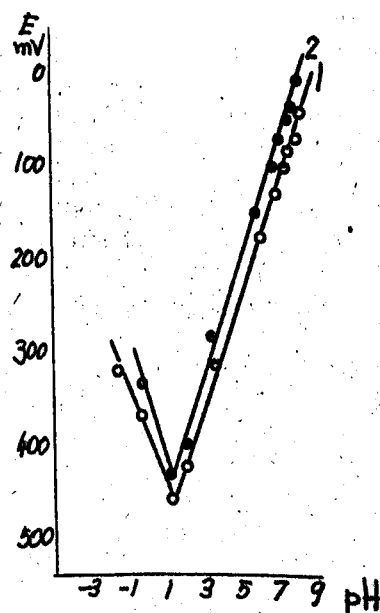


Fig. 3. Calibration curves of electrodes constructed of MacInnes and Dole glass against acetic acid solutions.

On comparing the calibration curves of glass electrodes in water and in acetic acid, we see that whereas an inflection point is observed at a pH of -0.2 for Hughes glass in acidic aqueous solutions, and merely a deviation from rectilinearity for Dole glass in the same pH region, in the acetic acid solutions

an inflection point is observed in the acidic region for both of the glasses at higher pH values of the order of +1.3. For Hughes glass the point of inflection is displaced by 1.5 pH units into the less acidic region, and the length of the negative portion of the calibration curve is increased in comparison with aqueous solutions.

As can be seen from the calibration curves for acetic acid solutions, between pH values of 1.5 and 8.5 (on the scale calibrated against the acetic acid standard) the potential of the glass electrode (constructed of both types of glass) changes rectilinearly with changing pH of solution.

We did not undertake studies in a more alkaline region since we could not attain higher pH values. Even a normal solution of sodium acetate in acetic acid has a pH of the order of 8, due to the low values of the activity coefficients of salts in acetic acid (dielectric constant of glacial acetic acid is 6.13 [8]).

The angular coefficient $\Sigma = \frac{\Delta E}{\Delta pH}$ in acetic acid solutions in the pH range of 1.5 to 8.5 has a mean value of 58.6 mV for Hughes glass and of 58.4 mV for MacInnes and Dole glass.

Consequently, for the acetic acid solutions which we examined in the pH range of 1.5 to 8.5 (on the scale related to the acetic acid standard) the glass electrodes may be used for measurements of acidity.

Reproducibility of Results During Measurements with the Glass Electrode in Acetic Acid

As is well-known, hysteresis is observed in the transition from alkaline to neutral solutions in aqueous and, particularly, in non-aqueous solutions. Hence, in order to assess the suitability of glass electrodes in acetic acid it was necessary to establish the degree of residual acidic hysteresis in the case of electrodes in acetic acid. With this objective in view, the electrodes were calibrated against acetic acid solutions starting from high pH values, and after the strongly acidic region they were at once again immersed in a solution with a pH of 8.3 and the series of measurements was repeated.

The experiment gave highly concordant results and pointed to the absence of residual acidic hysteresis in the alkaline region for glass electrodes in acetic acid.

The graphical representation of this double calibration in the case of Hughes glass electrodes is shown in Figure 4.

Immersion of the glass electrodes in water or measurement with the electrode of aqueous solutions immediately before measurements in acetic acid did not affect the electrode characteristics in acetic acid. This is clearly demonstrated in the following data for a Hughes glass electrode.

The values of E for a cell with a glass electrode in acetic acid solution with a pH of 6.05 are:

1. Immediately after keeping in water 0.5980 V
2. After measurement in aqueous solution for a period of 20 min.. 0.5980 V
3. After measurement in aqueous solution for a period of 65 min.. 0.5985 V
4. After immersion in acidic acetate solution for 40 min..... 0.5980 V

It follows that the constants of the glass electrode in acetic acid do not depend on the duration of immersion of the electrodes in water or on the sequence in which measurements are made.

Titration in Acetic Acid with the Glass Electrode

It follows from the present investigation that the glass electrodes can be used for titration in acetic acid. As an example we describe the titration of a

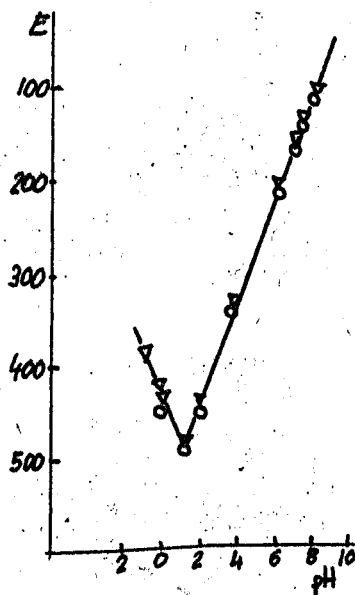


Fig. 4. Two repeated calibrations of a Hughes glass electrode.

On the graph the circles signify the first calibration and the triangles the second one.

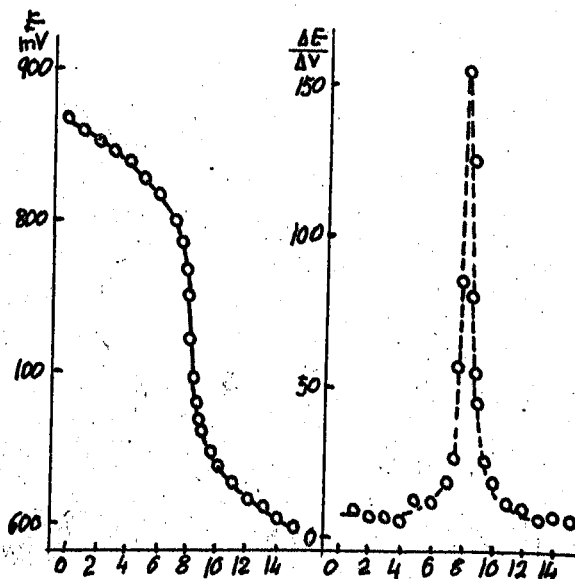


Fig. 5. Titration curves with a glass electrode in acetic acid.

solution of toluene sulfonic acid in acetic acid with an acetic acid solution of dimethylaniline, using a Hughes glass electrode.

Two calomel electrodes were included in the glass electrode cell:

Hg	Hg ₂ Cl ₂	Veibel's aqueous solution	Glass	Acetic acid solution under test	Saturated aqueous solution of KCl	Hg ₂ Cl ₂	Hg
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As siphon we used an agar-water bridge.

Titration proceeded smoothly and rapidly. The potential was established in the course of two minutes. The titration curves are shown in Figure 5. The titration curve obtained by plotting EmV against the number of milliliters of added dimethylaniline solution is represented by the heavy graph.

The differential curve (plot of $\Delta E/\Delta pH$ against the number (V) of milliliters of added dimethylaniline solution) is represented by the broken line.

It can be seen that these curves are typical titration curves. We recommend the glass electrode for the titration of any desired compounds in glacial acetic acid.

SUMMARY

1. A study was made of the behavior of glass electrodes in glacial acetic acid.

2. The suitability of glass electrodes for pH measurements in acetic acid solutions was demonstrated.

3. It was found that the point of inflection in the acidic region in acetic acid is displaced in the direction of higher pH values in comparison with aqueous solutions, and the negative branch of the curve becomes longer.

4. Glass electrodes are shown to be suitable for potentiometric titration in acetic acid.

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