BEHAVIOR OF A GLASS ELECTRODE IN NON-AQUEOUS MEDIA

IV. ERRORS OF THE GLASS ELECTRODE IN ACID AND ALKALINE REGIONS IN ETHANOL AND IN MIXTURES OF ETHANOL AND WATER

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As is known, the potential of a glass electrode varies linearly with the pH of a solution over a wide area. A deviation from rectilinearity is observed in strongly alkaline and acid regions. In the alkaline region, the glass electrode potential – solution pH curve, or what is the same, the calibration curve of the glass electrode at a certain pH value, deviates from rectilinearity and often passes through a maximum.

As was established by Nikolsky, the deviation from rectilinearity of the potential – solution pH curve in an alkaline region is explained by a shifting of the hydrogen function of the glass electrode to a sodium function; the length of the rectilinear portion of the glass electrode calibration curve being related, according to Nikolsky, [1] to the exchange constant K of the glass ions, where:

$$K = \frac{a_{H^+} \text{ of the solution } a_{Na^+} \text{ of the glass}}{a_{H^+} \text{ of the glass } a_{Na^+} \text{ of the solution}}$$

a_{H^+} and a_{Na^+} are the activities of the sodium and hydrogen ions in the glass and in the solution.

The location of the break in the Nikolsky calibration curve is also related to the value of the exchange constant for the glass ions. The formula for the glass electrode potential – glass constant curve has the following appearance:

$$E = E_0 + \frac{2.3RT}{F} \log \left(a_{H^+ \text{ solution}} + K a_{Na^+ \text{ solution}}\right)$$

where E and E_0 are the potential and null potential of the glass electrode.

From the literature data, a deviation from rectilinearity of the potential – solution pH curve is also observed in the acid region, but with a reverse sign to that of the alkaline region.

Having investigated the behavior of the glass electrode over a wide pH interval we observed for the first time not only a deviation from rectilinearity in a strongly acid region, but also the fact that the characteristic curve for the glass electrode passes through a minimum.

Examining the glass electrode as a membrane through which the hydrated hydrogen ions pass, Dole [2] explains the deviation in the acid region by the difference in activity of water on both sides of the membrane. Dole also expands his theory to non-aqueous solutions, maintaining that the ordinary glass electrodes cannot be used for measuring the activity of hydrogen ions in non-aqueous solutions. According

to Dole, the electrode reaction at the glass electrode can be written as follows:

$$H^{\circ}(n_1) + H_2O(P'_{H_2O}) \xrightarrow{H^{\circ}(H_2O)^{\circ}} H^{\circ}(n_2) + H_2O(P''_{H_2O}),$$

where $H^{\circ}(H_2O)^{\circ}$ is the hydrated proton. Then the equation for the glass electrode potential will take the form:

$$E = \frac{2.3RT}{F} \log \frac{a_1}{a_2} + \frac{2.3RT}{F} \log \frac{P'(H_2O)}{P''(H_2O)},$$

where P is the vapor tension of water.

Calculating the equation for the hydrogen electrode from the equation for the glass electrode, Dole found the magnitude of error of the glass electrode equal to:

$$\Delta E = \frac{2.3RT}{F} \log a_{H_2O},$$

where $a_{H_2O} = \frac{P'(H_2O)}{P''(H_2O)}$ – the activity of water in the external solution.

And consequently for an anhydrous medium, in particular for anhydrous ethyl alcohol where the activity of water becomes negligible, but where an aqueous solution is contained inside the electrode, the error reaches such a magnitude that the glass electrode cannot be used for measurement.

Dole then draws the conclusion that the glass suitable for work in non-aqueous solutions should allow only unhydrated hydrogen ions to pass through.

As a result of experimental investigations in 1938 Izmailov and Belgova [3] found that in alcoholic mixtures containing 50 and 70% ethyl alcohol and at a pH interval of 4 to 8, the glass electrode behaves exactly as in aqueous solution.

Later, Izmailov and Frantsevich-Zabludovskaya [4], investigating the behavior of glass electrodes, made from electrode glass of the usual composition, in mixtures of ethyl alcohol and water, in acetone mixtures and in 90% methyl alcohol, showed that the glass electrode was fully suitable for the measurement of pH in non-aqueous solutions.

We continued the investigation of the behavior of the glass electrode in water and in mixtures of ethyl alcohol and water, up to absolute ethyl alcohol. In each case the glass constant was calculated, and this done, a relationship was found between the constant measured and the molarity of the alcohol in the mixture. We also calibrated the glass electrode with buffered solutions in absolute methyl alcohol.

EXPERIMENTAL

Alkaline Region

In our work we conducted an investigation of the behavior of glass electrodes in the media shown in Table 1.

We used these alcohol-water mixtures since their HCl activity coefficients were known.

We investigated glass of three different compositions. The compositions of the glass are given in Table 2.

Spherical electrodes were prepared from the glass, according to Haber. In all cases the inside of the electrodes was filled with an aqueous Weibel solution. The prepared electrodes were submerged in 0.1 N HCl for 3 - 5 days. Thereafter the electrodes were stored in distilled water.

TABLE 1

Expt. No.	Solvent (% by weight)	Molar fraction of the solution	pH intervals
1	Water	–	– 0.9 + 14.0
2	20 ethanol	0.0891	– 0.8 + 14.3
3	71.9 ethanol	0.5	– 0.6 + 14.86
4	88.5 ethanol	0.75	– 0.5 + 15.56
5	93.5 ethanol	0.85	– 0.5 + 15.85
6	100.0 ethanol	1.0	+ 0.6 + 14.1
7	100.0 methanol	1.0	+ 0.9 + 15.8

TABLE 2

Expt. No.	Type of glass	Composition of the glass (in %)				
		SiO_2	Na_2O	CaO	R_2O_3	Remainder
1	Yuz glass	72.0	20.0	8.0	–	–
2	McInnes and Dole Glass (Corning 015)	72.0	22.0	6.0	–	–
3	"Eldaf" 4 glass	66.93	22.84	4.92	0.55	4.76

Measurements with the glass electrodes were carried out with a vacuum-tube amplifier in conjunction with a Raps potentiometer, the construction of which is described in detail by Izmailov and Zabara [5].

The composition of the cell, during measurement of aqueous solutions and mixtures of alcohol and water by means of the glass electrode, was the following:

Hg	$\frac{Hg_2Cl_2}{KCl_{sat.}}$	$KCl_{sat.}$	Investigated solution	Glass	Weibel's aqueous solution	Weibel's Hg_2Cl_2 solution	Hg

In the case of absolute methyl and ethyl alcohols, the aqueous calomel electrode and the aqueous bridge was eliminated from the cell. All the measurements were conducted in a circuit with a quinhydrone electrode placed in an alcoholic solution which served as a standard half-cell and consisted of 0.01 N HCl and 0.009 N NaBr.

Contact was accomplished by means of a bridge filled with a saturated solution of KBr in absolute alcohol.

For calibrating the glass electrodes in water, a series of buffer solutions was prepared: according to McElvain, pH 2.7-8.0; according to Sorensen, pH 9.3-10.1; and according to Ringer, pH 11.3-12.3. For higher pH values solutions of sodium hydroxide were used.

In a strongly acid region (pH from -1 to +2) the electrodes were calibrated with hydrochloric acid solutions.

A series of buffer solutions, mixtures of an acid and its salt, were prepared in ethanol-water mixtures and in absolute ethyl and methyl alcohols (Li salt was used for absolute ethyl alcohol and sodium salt for all the other cases).

The composition of the buffer solutions are shown in Table 3. For the more alkaline regions, solutions of sodium hydroxide were prepared in mixtures of ethyl alcohol and water and in solutions of sodium alcoholate in absolute alcohols, having the pH values shown in Table 3.

TABLE 3

Expt. No.	Buffer	Concentration acid	Concentration salt	Ethyl alcohol (% by weight) 20.0	71.9	88.5	93.5	100.0	Methyl alcohol 100%
				pH of the buffer solutions					
1	Trichloroacetate	0.1	0.1	–	–	–	–	4.0	4.0
2	Salicylate.....	0.1	0.01	3.4	3.8	4.56	5.0	5.9	6.0
3	Salicylate.....	0.01	0.1	5.1	5.6	6.24	6.8	8.1	–
4	Benzoate.....	0.1	0.1	5.7	6.3	6.9	7.4	–	8.4
		0.01	0.1	6.6	7.3	8.0	8.4	–	–
5	Veronalate.....	0.1	0.01	8.2	8.7	9.3	9.8	11.5	10.1
		0.001	0.1	9.6	10.1	10.7	11.3	12.7	12.4
6	Phenolate.....	0.1	0.01	10.0	10.9	11.5	12.0	13.4	12.2
		0.1	0.1	11.3	12.0	12.6	12.9	14.1	13.4
				pH of the alkaline solutions					
7	Solutions of sodium hydroxide or sodium alcoholate.....	–	–	14.3	14.86	15.56	15.85	–	14.0 14.4 15.8

The pH of all the solutions was measured with a hydrogen electrode in a concentration cell relative to the standard, a 0.1 N HCl in the corresponding solvent; i.e., the standard was an infinitely diluted solution of ions in the given medium and not in water.

The pH values were calculated from the data on the activity coefficients of 0.1 N HCl [5]. In the case of the alcohol-water mixtures the calculation was made according to the formula:

$$\log a = \frac{E_0 - E}{0.1154} \text{ at } 18°$$

and consequently, $pH = \frac{E_0 - E}{0.1154}$. The values for the E and E_0 used in our cells were taken from the work of Harned [6].

The glass electrodes were first calibrated by aqueous buffer solutions. The results of the calibration were plotted graphically, as the potential – solution pH curve. The calibration curves for Yuz glass and MacInnes and Dole glass in aqueous buffer solutions are given in Figs. 1 and 2. The calibration curve for "Eldaf" glass has an identical appearance. As is evident from the diagrams, the break in the curve for all three glasses lies at pH ≈ 113.1.

Nikolsky and Tolmacheva [7] proposed to calculate the exchange constant of the glass ions by the position of the maximum on the calibration curve of the glass electrode. The equation they proposed is of the form:

$$-\log K = 2pH_{max} - pK_i ,$$

where pH_{max} is the pH value at the break point of the calibration curve, and pK_i is the ion product of the medium.

Having substituted the pH_{max} values of the calibration curves in the equation, we found that the value for the exchange constant of the glass ions for all three glasses in water was $K = 6.31 \cdot 10^{-13}$.

The glass electrodes were then calibrated in the above-mentioned alcohol-water solutions. The results of the calibration were plotted using the same coordinates. In order to obtain a more coherent picture of the influence of the alcohol content in the solution on the calibration curve of the glass electrode, the calibration

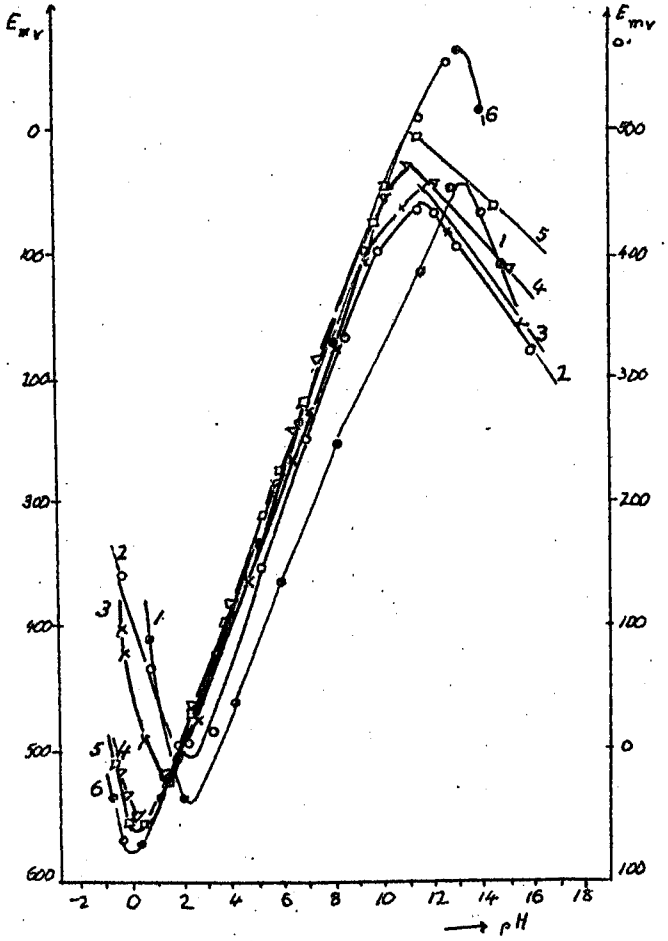

Fig. 1. Calibration curves for a glass electrode made from Yuz glass in ethanol-water mixtures and in absolute alcohol.
Ethyl alcohol: 1 - 100%; 2 - 93.5%; 3 - 88.5%; 4 - 71.9%; 5 - 20.0%. 6 - Water.

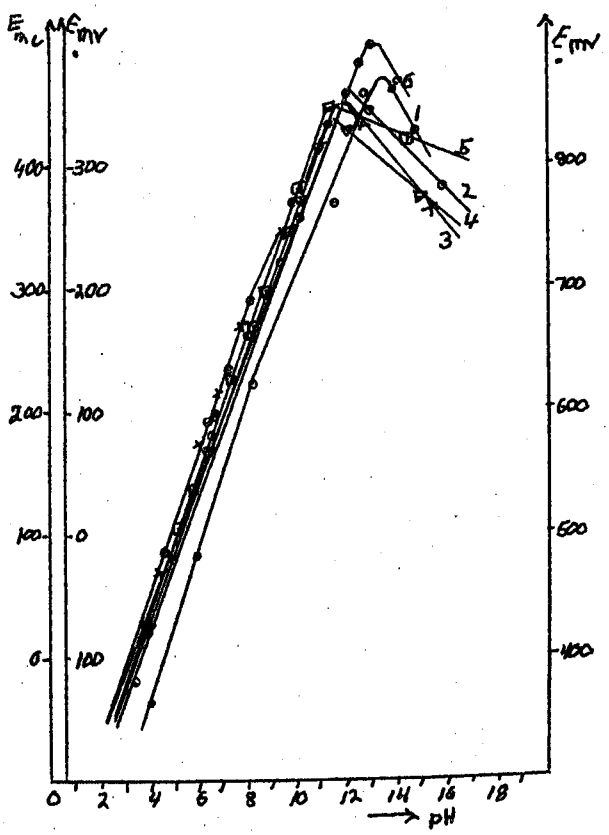

Fig. 2. Calibration curves for a glass electrode made from MacInnes and Dole glass in ethanol-water mixtures and in absolute ethyl alcohol.
Ethyl alcohol: 1 - 100.0%; 2 - 93.5%; 3 - 88.5%; 4 - 71.9%; 5 - 20.0%. 6 - water.

results of the entire series of solutions were plotted on the same graph, but one graph for each glass, on Fig. 1 – for the electrode made from Yuz glass and on Fig. 2 – for the electrode made from MacInnes and Dole glass.

As is evident from the results of the measurements, an increase in the percent of alcohol in the alcohol-water mixtures shifts the position of the break in the calibration curve towards the direction of the higher pH values. Thus, for example, if for 20% ethyl alcohol the break on the calibration curve of the glass electrode made from Yuz glass lies at $pH_{max} = 11.0$, then for 93.5% ethanol, $pH_{max} = 11.65$. The same situation is observed for MacInnes and Dole glass, but the displacement is somewhat greater.

It should also be pointed out that the deviation from the rectilinear relationship between the potential of the glass electrode and the pH of the solution occurs much sooner for those calibration curves corresponding to a higher alcohol content. Consequently, an increase in the content of alcohol in the solution leads to a

decrease in the rectilinear portion of the calibration curve, which results in a restriction of the range in which the glass electrode may be used for the measurement of pH in ethanol-water mixtures and in absolute alcohol.

Having constructed the calibration curves of the glass electrode in the alcohols, and having consequently obtained the value for pH_{max}, we calculated the values for the exchange constants of the glass ions in the corresponding mixtures of water and ethyl alcohol, using the Nikolsky and Tolmacheva formula. We obtained the values for the ion product of the medium, necessary for calculation of K, from a graph constructed from Kilpi's data [8]. The values for pK_i were then found to be the following:

	pK_i
100.0% (by weight) ethyl alcohol ...	20.2
93.5% ...	17.35
88.5% ...	16.8
71.9% ...	15.74
20.0%	14.25

The results of our calculations for the exchange constants of the glass ions are given in Table 4.

If, in accordance with this data, the value of pK_i for absolute ethyl alcohol is taken to be equal to 19.4, then the constant of Yuz glass in absolute ethanol will be equal to $1.26 \cdot 10^{-7}$, and MacInnes and Dole glass equal to $0.3 \cdot 10^{-7}$.

As is evident from the above table, the value for pH_{max} shifts to the more alkaline region with increase in ethyl alcohol content. The value of the glass constant sharply increases on addition of a small quantity of alcohol to the water. Thus, if K of the glass is equal to $6.3 \cdot 10^{-13}$ in water, then in an alcohol-water mixture containing 0.089 molar parts of ethyl alcohol, the K for Yuz glass is equal to $1.78 \cdot 10^{-8}$ and K for MacInnes and Dole glass is equal to $8.9 \cdot 10^{-9}$. By such a tiny addition of ethyl alcohol to the water, the glass constants increase 4-5 exponential units. On changing from the ethanol-alcohol mixture containing 0.089 mol. parts of alcohol to a mixture containing 0.5 mol. parts of ethyl alcohol, the constant increases approximately ten times. But in alcohol-water mixtures with higher and contiguous contents of ethanol, the constant practically does not change either for Yuz glass or for MacInnes and Dole glass.

If the value of the glass constant is compared in water and in absolute ethanol it may be seen that the constant in absolute ethyl alcohol, for both glasses, is greater than the glass constant in water by 6 exponential units.

We also calibrated the glass electrodes made from these glasses in absolute methyl alcohol. A graphical representation of the calibration is shown on Fig. 3. In this case the value of pH_{max} for Yuz glass is equal to 13.3 and for MacInnes and Dole glass it is equal to 13.8. Taking the ion product of absolute methyl alcohol equal to 17.05, we find the value for K for both glasses from the Nikolsky and Tolmacheva formula: for Yuz glass: $K = 2.82 \cdot 10^{-10}$ and for MacInnes and Dole

TABLE 4

Expt. No.	Percent Ethanol (by weight)	Yuz glass		MacInnes and Dole glass		"Eldaf" glass	
		pH_{max}	K	pH_{max}	K	pH_{max}	K
1	100.0.....	13.1	$8.10 \cdot 10^{-7}$	18.45	$2.0 \cdot 10^{-7}$	–	–
2	93.5	11.6	$1.12 \cdot 10^{-6}$	12.10	$1.41 \cdot 10^{-7}$	12.0	$2.24 \cdot 10^{-7}$
3	88.5	11.4	$7.9 \cdot 10^{-7}$	11.80	$1.58 \cdot 10^{-7}$	11.5	$6.31 \cdot 10^{-7}$
4	71.9	11.1	$2.75 \cdot 10^{-7}$	11.45	$6.91 \cdot 10^{-8}$	–	–
5	20.0	11.0	$1.78 \cdot 10^{-8}$	11.15	$8.91 \cdot 10^{-9}$	–	–
6	0.0 (water)..	13.1	$6.31 \cdot 10^{-13}$	13.10	$6.31 \cdot 10^{-13}$	13.1	$6.31 \cdot 10^{-13}$

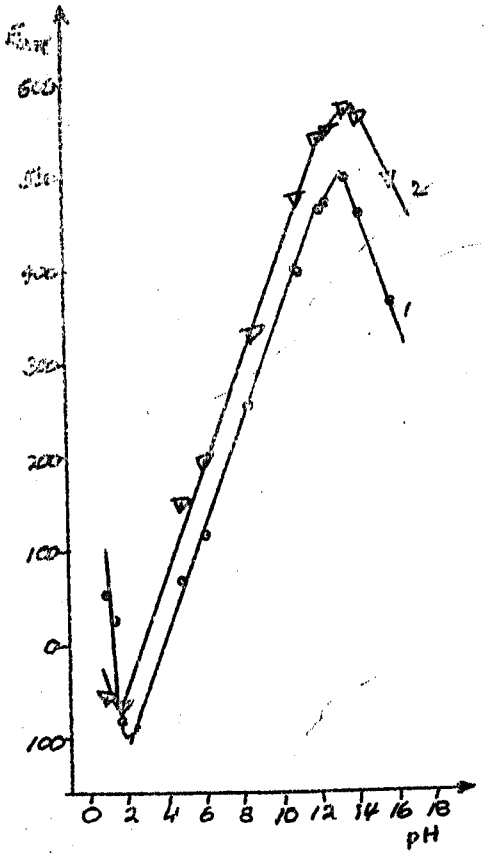

Fig. 3. Calibration curves of glass electrodes in absolute methyl alcohol. 1 - Yuz glass; 2- MacInnes and Dole glass.

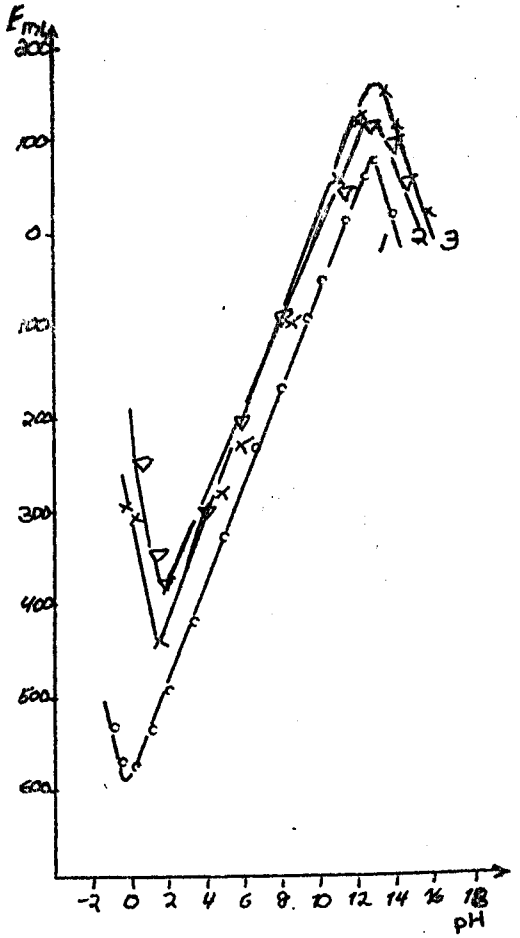

Fig. 4. Calibration curves of a glass electrode made from Yuz glass in absolute alcohols and in water. 1 - in water; 2 - in absolute ethyl alcohol; 3- in absolute methyl alcohol.

glass $2.82 \cdot 10^{-11}$. Izmailov and Frantsevich-Zabludovskaya [9] present data in 90% (by weight) of methyl alcohol for Yuz glass. They found the pH_{max} equal to 13.2 and the value of K equal to $3.98 \cdot 10^{-12}$ at $pK_1 = 15$; i.e., the value for the glass constant in absolute methyl alcohol is greater than in methanol-water mixtures. On the basis of the foregoing it may be concluded that the exchange constant of glass ions increases on changing from water to alcohol-water mixtures and further increases on changing to absolute alcohols.

We were also interested in the question of the relationship of the magnitude of the potential for the same glass electrode in different media at equal pH values. In the work of Izmailov and Frantsevich-Zabludovskaya [4], data are cited for measurement with the same glass electrode in aqueous solutions, in 95% ethyl alcohol and in 90% methyl alcohol. According to their data, the fluctuations observed in the potential of the glass electrode result only from changes in external conditions.

We conducted measurements of aqueous solutions and buffer mixtures in absolute ethyl and methyl alcohols with the same electrode. Since a saturated calomel electrode was substituted by a quinhydrone in the absolute alcohols for the experiments where the absolute alcohols were used in a variable cell with a glass electrode,

it is natural that the observed potentials of both cells were not commensurate. In this case we calculated the potentials of the quinhydrone electrodes in the ab absolute alcohols. The values for E_0 in the absolute alcohols were taken from Br Brodsky's monograph [10].

We shifted the position of the calibration curves to correspond to the difference in potentials between the aqueous saturated calomel electrode and the quinhydrone electrode in absolute alcohol. As is evident from Fig. 4, the calibration curves are situated close to each other. The amount by which the calibration curves differ may be explained by the difference in phase and diffusion potentials. It is quite evident from Fig. 5 that the potentials coincide at the medial pH values for electrode No. 2, made from MacInnes and Dole glass placed in aqueous buffer solutions and in buffer solutions in 88.5% ethyl alcohol. The calibration of the electrodes was conducted under identical conditions. As is evident in this case, the calibration curves coincide at the rectilinear portion.

As a result of these experiments it can again be confirmed that the potential of a glass electrode at medial pH values does not depend upon the medium in which the measurement is conducted.

Acid Region

At the present time there is very little data in the literature on the behavior of the glass electrode in the acid region in aqueous solutions and still less in the acid region in non-aqueous media.* We investigated the behavior of glass electrodes in acid and strongly acid regions in water, in ethanol-water mixtures and in absolute ethyl and methyl alcohols. The electrodes made from Yuz glass and from MacInnes and Dole glass were calibrated.

With this aim in mind, hydrochloric acid solutions were prepared in water and in alcohols. The pH of the hydrochloric acid solutions was determined by the hydrogen electrode relative to a standard. As in previous measurements, the standard was a 0.1 N solution of hydrochloric acid in the corresponding medium.

The results for the calibration of glass electrodes in the above solutions of hydrochloric acid are given on Fig. 1 for Yuz glass. As may be observed from Fig. 1, the calibration curve for the electrode has two breaks: a maximum in the alkaline region and a minimum in the acid region. The deviation in the acid region has a reverse sign in relation to the deviation in the alkaline region. It should be noted that in the works on the glass electrode presented in the monographs of Bchelin [11] and Dole [2], mention is made only of the deviation from rectilinearity of the calibration curve in the acid region.

Measurement with a glass electrode in strongly acid solutions is very difficult. The potential is not well established in the extremely acid point of the field. Electrodes made from Yuz glass – wetted for 2-3 days as well as for a longer period of time – give, in all cases, a minimum in the acid region. The position of the minimum then shifts to a less acid region on changing from water to absolute alcohol, which is easily seen from Table 5. As concerns MacInnes and Dole glass, we cannot cite analogous data. Some of the electrodes, wetted for a longer period of time, showed a minimum on the calibration curves. The calibration curves for electrodes prepared a long time before calibration just exhibited a strong deviation from rectilinearity. Even for those electrodes which showed a minimum on the calibration curve, the position of the minimum did not change on varying the solution investigated, and remained at all times at a pH of -0.5.

Shifting the position of the minimum as well as the previously-mentioned deviation of the calibration curve from rectilinearity shorten the rectilinear portion of the calibration curve as the alcohol content increases. In Table 6 is given the relationship of the magnitude of the rectilinear portion of the calibration curve

*The behavior of the glass electrode is practically unknown in strongly acid non-aqueous solutions.

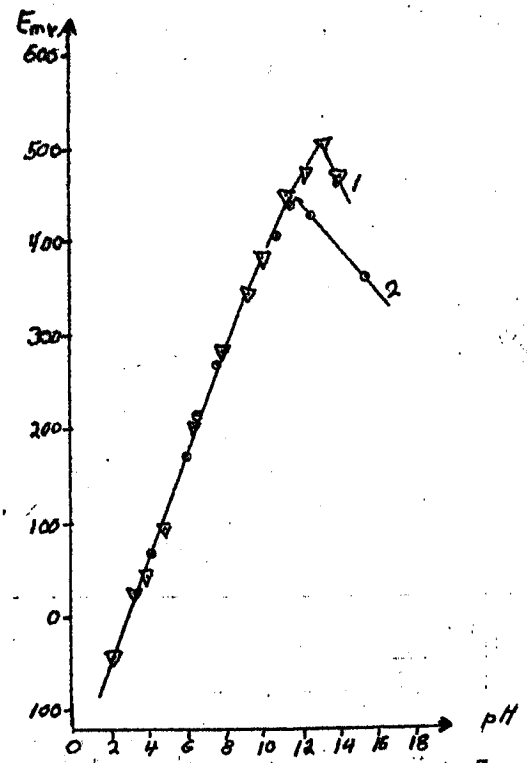

Fig. 5. Calibration curves of a glass electrode made from MacInnes and Dole glass in water and in 88.5% ethyl alcohol.
1 - water; 2 - 88.5% ethyl alcohol.

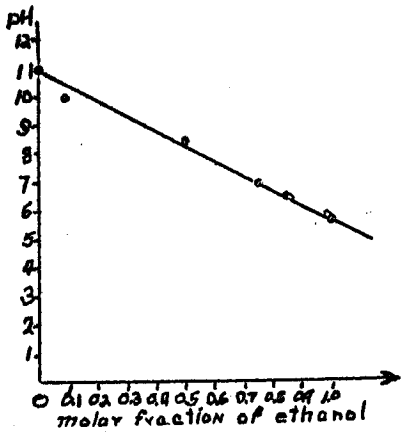

Fig. 6. Relationship of the magnitude of the rectilinear portion of the calibration curve, for the glass electrode made from Yuz glass, to the molar fraction of ethyl alcohol.

to the molar fraction of ethyl alcohol in ethanol-water mixtures. The data of Table 6 is represented on Fig. 6.

TABLE 5

Exp. No.	Solution	pH
1	Water.....	-0.2
2	20% (by wt.) ethanol.	0.0
3	71.9%	+0.3
4	88.5%	+1.2
5	100.0%	+2.2
6	100.0% methanol.....	+1.9

Available experimental data is still too meager to make general conclusions on the behavior of the glass electrode in the acid region, in particular in an acid region of non-aqueous solutions, but this question deserves attention.

Relationship of the Glass Electrode Potential to the Absolute Acidity

Of especial interest is the representation of our results by the universal scale pA, which is standardized against an infinitely diluted solution of the acid ions in aqueous solution by the use of the average activity coefficient. The universal scale pA, proposed by N.A.Izmailov [12], differs from the pH scale by the value lg γ_0:

$$pA = pH - \log \gamma_0,$$

where γ_0 is the average coefficient of the ions at infinite dilution in the given medium, referred to an infinitely diluted aqueous solution of the ions as a standard. The value log γ_0 for ethyl alcohol is shown in Table 7.

The calibration curves for glass electrodes made from Yuz glass are shown in the pA scale on Figs. 7 and 8 (for acid and alkaline regions respectively). Glass electrodes made from MacInnes and Dole glass give analogous calibration curves, which exhibit a contraction of the minima and maxima in the pA scale.

TABLE 6

Exp. No.	Molar fraction of ethanol	Length of the rectilinear portion for Yuz glass in pH units
1	0.0 (water)	10.9
2	0.0891	9.8
3	0.5	8.4
4	0.75	6.9
5	0.85	6.4
6	1.0	5.6

TABLE 7

Exp. No.	Molar fraction of ethanol	log Y_o
1	0.089	0.127
2	0.5	0.597
3	0.75	1.034
4	0.85	1.27
5	1.0	2.32

As may be seen from Fig. 7, on shifting the calibration curve for absolute alcohol to the acid region it approaches a pA value of -1.7. As is evident from the diagrams, the minima and maxima of the calibration curves in different alcohol-water mixtures, using the pA scale, lie along one straight line and tend to coalesce.

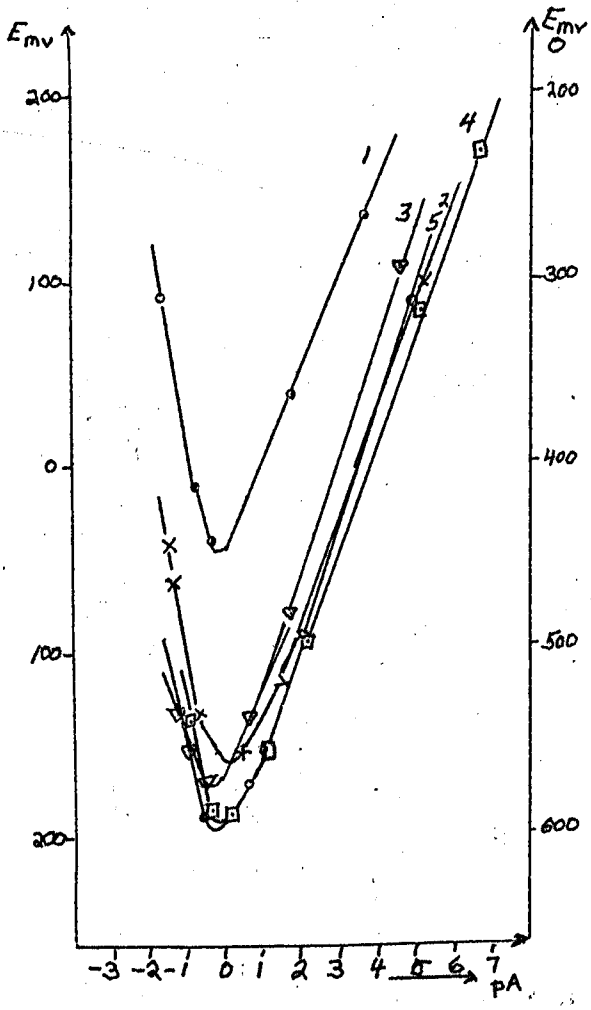

Fig. 7. Calibration curves of glass electrode made from Yuz glass using the universal scale. Acid region. Ethyl alcohol: 1- 100.0%; 2- 88.5%; 3 - 71.9%; 4 - 20.0%; 5 - water.

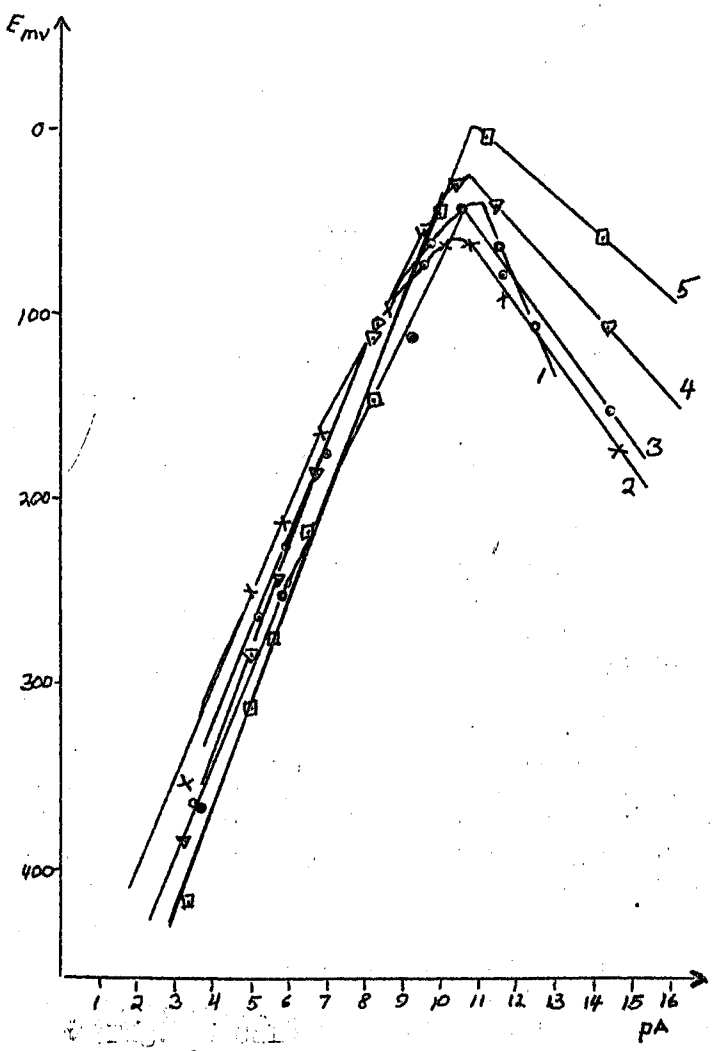

Fig. 8. Calibration curves of a glass electrode made from Yuz glass using the universal scale. Alkaline region. Ethyl alcohol: 1 - 100.0%; 2 - 93.5%; 3 - 88.5%; 4 - 71.9%; 5 - 20.0%.

This consequently indicates that the errors of the glass electrode in acid and alkaline regions are fractions of the total acidity of the medium.

It should be noted that since 1941 we conducted all the experimental work with our own glass furnace.

We wish to take this opportunity to express our deep gratitude to V.A.Pchelin for his kindness in providing us with electrode glass.

SUMMARY

1. An investigation of the behavior of glass electrodes made from Yuz glass and MacInnes and Dole glass was conducted in ethanol-water mixtures and in absolute ethyl and methyl alcohols. It was established that in all these solutions the calibration curve of the glass electrode contains a maximum in the alkaline region. With increase in ethyl alcohol content, the position of the maximum shifts to a more alkaline region.

2. In an acid (hydrochloric acid) region a deviation is observed from the rectilinear potential – solution pH curve, which has a reverse sign to the deviation of the alkaline region, both for aqueous solutions as well as for alcohols. The calibration curve for a glass electrode made from Yuz glass possesses a minimum in the acid region. The position of the minimum, as well as the beginning of deviation from rectilinearity, shifts to a less acid region from water to absolute ethyl alcohol.

3. The value, K, of the exchange constant for glass ions increases on shifting from water to absolute alcohols. If for water, the K of the investigated glasses equals $6.31 \cdot 10^{-13}$, then in absolute ethyl alcohol the K for Yuz glass equals $8.0 \cdot 10^{-7}$ and for MacInnes and Dole glass equals $2.0 \cdot 10^{-7}$. In absolute methyl alcohol the value of K for Yuz glass is equal to $2.82 \cdot 10^{-10}$, and for MacInnes and Dole glass it is equal to $2.82 \cdot 10^{-11}$.

4. The use of the glass electrode for measuring pH in mixtures of ethyl alcohol and water and of absolute ethyl and methyl alcohols is quite practical, but with an increase in the alcohol content the region of applicability of the glass electrode is curtailed.

5. It was shown that the errors of the glass electrode in acid and alkaline regions are situated at the same value of the absolute acidity, pA.

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