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HYGROSCOPICITY AND ELECTRODE FUNCTION (pH RESPONSE) OF GLASSES AS A MEASURE OF SERVICEABILITY

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ABSTRACT

The pH responses of electrodes prepared from glasses of widely different composition have been compared with the hygroscopicity of the glasses. The resulting data indicate that glasses of low hygroscopicity, such as the chemical glasswares and common types of optical glasses, give pH responses that fall appreciably below the theoretical predicted from the Nernst equation and are incapable of producing satisfactory electrodes. Further, electrodes blown from glasses of intermediate hygroscopicity, such as the common bottle and sheet glasses, give pH responses more nearly approximating the theoretical, whereas the Corning 015 glass, whose superior pH response places it in a class by itself, has a very high hygroscopicity. These results strongly support the belief that adequate hygroscopicity is one of the primary factors in determining the suitability of a glass for pH measurements. The data also suggest that the pH response might well be used as a rapid test for the serviceability of optical glasses, i. e., the ability to maintain a clear polished surface upon exposure to the atmosphere. For this purpose it is necessary to determine the pH response over a range in which the "chemical durability" of the glass remains constant in order to avoid the voltage anomalies that accompany durability changes.

CONTENTS

I. INTRODUCTION

The ability of a glass to function satisfactorily as an indicator of hydrogen-ion concentration, approximately in accord with the straight-line relation of the simplified Nernst equation,[1] is known to

[1] $E=0.000198T \log 1/[H^+]=0.000198TpH$, where E is emf, T is temperature degrees Kelvin, $pH=\log 1/[H^+]$, and $[H^+]$ denotes hydrogen-ion concentration or activity.

be intimately associated with the water content of the glass [1, p. 78].[2] As the serviceability of an optical glass, i. e., its ability to maintain a clear polished surface upon exposure to the atmosphere, has been shown to be largely dependent upon the hygroscopicity of the glass [2], it seems reasonable to believe that the serviceability might also be ascertained easily and quickly, at least qualitatively, by a determination of its hydrogen-electrode function.

In the present investigation the hygroscopicity and pH response were observed on a series of glasses of varying serviceability and a comparison was made of the data obtained on these properties.

II. TYPES OF GLASSES

A selection was made of 12 glasses that exhibited a wide range in serviceability. Vycor and Pyrex were chosen as glasses of superior serviceability, whereas the Dish and Corning 015 were selected because they had not maintained clear surfaces upon exposure to the atmosphere. The compositions of 11 of these glasses are given in table 1.

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[2] Figures in brackets indicate the literature references at the end of this paper.

TABLE 1.—*Percentage compositions of glasses tested for hygroscopicity and pH response*

Glass	SiO_2	B_2O_3	P_2O_5	SO_3	Al_2O_3	As_2O_3	Sb_2O_3	PbO	ZnO	CaO	MgO	BaO	K_2O	Na_2O	R_2O_3
Corning 015 [a]	72.0									6.0				22.0	
Dish [b]	72.7		0.12		0.54	0.09	0.18			9.3		0.4		16.6	
Goblet [b]	66.1							17.2				1.4	9.7	5.6	
Am. Ceram. Soc. No. 1	73.27									4.85	3.3		[f] 16.68		1.06
Window	72.1			0.35						10.0	3.3			13.5	0.7
Electric hygrometer (soft-glass tubing) [c]															
Blue bottle	77.5	0.5								5.6			[f] 12.9		3.5
BSC 517 [d]	66.4	12.4				.5			0.5				11.8	8.4	
F 620 [d]	45.6					.5		45.1					5.2	3.6	
BaC 572 [d]	49.7	3.6				.2	.4		7.2			30.8	7.7	.4	
Pyrex [e]	81.0	13.0				.002							.2	3.6	2.2
Vycor [e]	96.3	2.9											$<.02$	$<.02$	.4

[a] D. G. MacInnes and M. Dole, The behavior of glass electrodes of different compositions, J. Am. Chem. Soc. **52**, 29–36 (1930).
[b] Contributed by A. E. Williams.
[c] Francis W. Dunmore, An electric hygrometer and its application to radio meteorography, J. Research NBS **20**, 723 (1938) RP1102.
[d] Optical glasses.
[e] Analyses made by Francis W. Glaze.
[f] K_2O and Na_2O combined.

III. EXPERIMENTAL PROCEDURE

The hygroscopicity data were obtained from the weight of the water sorbed by powdered samples of the glasses that passed The Tyler Standard Sieve No. 150. This powder was exposed to the relative humidity, approximately 95 percent, maintained by a saturated solution of $Na_2HPO_4.12H_2O$[3] at 25°C. During the sorbing period of 16 hours the air was circulated continuously in the exposure chamber by means of a small fan.

The hygroscopicity values for all of the glasses are reported in terms of known factors, namely, weight of water sorbed times density of the glass divided by weight of sample. Assuming comparable sieving and preparation of the samples, this gives the water sorbed for equal surfaces.

The glass electrodes were prepared by blowing a small, thin bulb of the experimental glass on the end of a soft glass tube or from a tube of the glass itself [4] and filling the bulb with mercury for the electrical connection [3]. Although metal-filled glass electrodes are not considered as suitable for precise work as the solution-filled types, they were entirely satisfactory for the present investigation and had the advantage of simplicity and speed of preparation. Further, a broken electrode did not seriously contaminate or alter the buffer solutions.

All voltage and pH measurements were made with a Beckman pH meter, laboratory model G. The sensitivity of this type of electrometer decreases appreciably for electrodes with resistance greater than 500 megohms, and as many of the electrodes prepared from the glasses of low hygroscopicity had resistances above this value, it is desirable to consider the pH responses obtained as "apparent" pH responses.

IV. RESULTS AND DISCUSSION

1. pH RESPONSE IN THE ACID RANGE

The silicate glasses, table 1, were measured for hygroscopicity, and their hydrogen-electrode function (pH response) was determined after soaking the electrodes 24 hours in distilled water. The results in table 2 show the relation between hygroscopicity and the pH response obtained with two buffer solutions near pH 2 and pH 4. These two pH values were chosen because they are in the region of uniform chemical durability for most silicate glasses [4]. This procedure was desirable in order to avoid voltage anomalies that accompany durability changes of the glass [5].

From the data in table 2 it is evident that the pH response of the glasses with low hygroscopicity falls appreciably below the theoretical predicted from the Nernst equation, and that the pH responses for these glasses are in the same order as their respective hygroscopicities. During these experiments it was observed that the glasses improve in their pH response when soaked in distilled water [6]. This improvement was especially noticeable for the glass BaC 572.

[3] The relative humidity obtained by means of a saturated salt solution is subject to some fluctuation because of the difficulty of obtaining equilibrium rapidly and because of the decrease in relative humidity that occurs when a crust of the salt forms over the surface of the solution. However, this method does furnish an easy means of comparing the relative hygroscopicities of a number of glasses.

[4] Tubes of the experimental glasses were drawn by Thomas R. Tait, of the Bureau's glass-blowing shop.

TABLE 2.—*Comparison of hygroscopicity and* pH *response at 25° C of some typical commercial and optical glasses, after soaking the electrodes in distilled water for 24 hours*

Glass	Water sorbed	pH response
	mg per cm ^{3}	*mv per* pH
Corning 015	358	59
Dish	88	58
Am. Ceram. Soc. No. 1	40	57
Window	39	56
Electric hygrometer	39	56
Blue bottle	30	54
BSC 517	5.5	43
F 620	4.8	39
BaC 572	2.2	33
Pyrex	1.8	18

In order to observe the effect of time on pH response another set of electrodes was prepared from six of the typical glasses used in the previous series plus two others, and emf measurements were taken at intervals for 27 days. The data are given in table 3. The pH response for each of these glasses, immediately after preparation, is plotted against the hygroscopicity in figure 1, and the change in pH response with time is shown in figure 2. Figure 1 shows that the glasses fall in their correct order of hygroscopicity similar to the data in table 2 and reemphasizes the finding that the pH response increases very rapidly with increase in the hygroscopic property of the glasses. The numerical values for the second set of electrodes do not agree exactly with those of the first group. In order to obtain exact reproducibility, successive electrodes of the same glass would have to be of equal thickness to maintain identical electrical resistance. This is especially pertinent for glasses of high electrical resistance. Further, in blowing the electrodes the composition of the outer surface of the glass is altered by volatilization of some of the consitutents of the glass by the blast lamp, and as the points for the less hygroscopic glasses lie on the steep portion of the curve, slight changes would cause correspondingly large changes in pH response. Furthermore, the electrodes prepared from these less hygroscopic glasses are sluggish, causing some uncertainty as to the correct reading.

TABLE 3.—*Comparison of hygroscopicity and* pH *response at 25° C of some typical commercial and optical glasses after soaking the electrodes for various lengths of time in distilled water*

Glass	Water sorbed	pH response, mv per pH. Time of soaking, days—										
		0	1	2	3	4	5	6	11	16	20	27
	mg/cm^3											
Corning 015	358	59.0	59.1	59.1	------	59.2	------	59.1	59.6	59.4	59.4	59.4
Dish	88	57.4	58.7	59.2	------	------	------	------	------	------	------	------
Am. Ceram. Soc. No. 1	40	56.0	56.5	57.6	------	58.5	------	58.9	59.1	58.9	59.0	58.8
Goblet	20	51.7	53.0	------	------	------	54.3	------	54.7	------	------	54.1
BSC 517	5.5	48.3	50.4	51.4	------	------	------	52.9	52.1	51.7	51.4	49.2
BaC 572	2.2	33.7	49.1	------	52.6	53.2	53.1	------	53.9	54.1	52.5	50.5
Pyrex	1.8	11.8	12.5	12.6	15.4	14.4	------	12.9	14.2	14.0	13.9	14.5
Vycor [a]	0.8	------	------	------	------	------	------	------	------	------	------	------

[a] Developed no definite pH response.

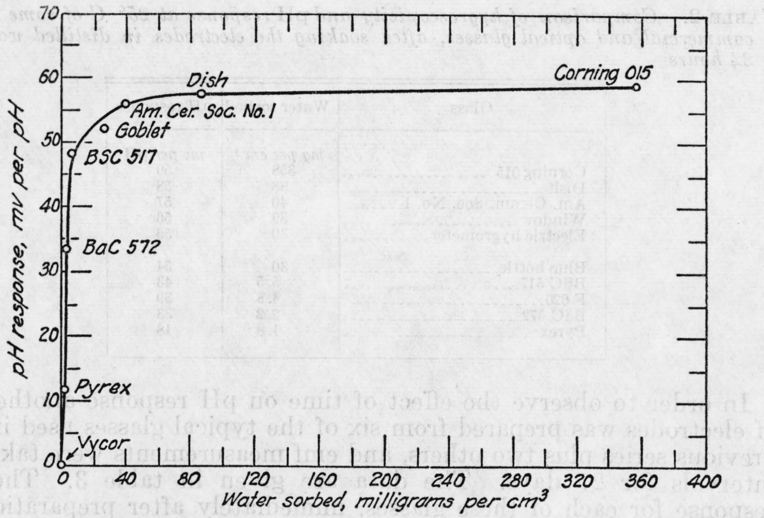

FIGURE 1.—*Comparison of hygroscopicity and pH response of some typical commercial and optical glasses immediately after preparation of the electrodes.*

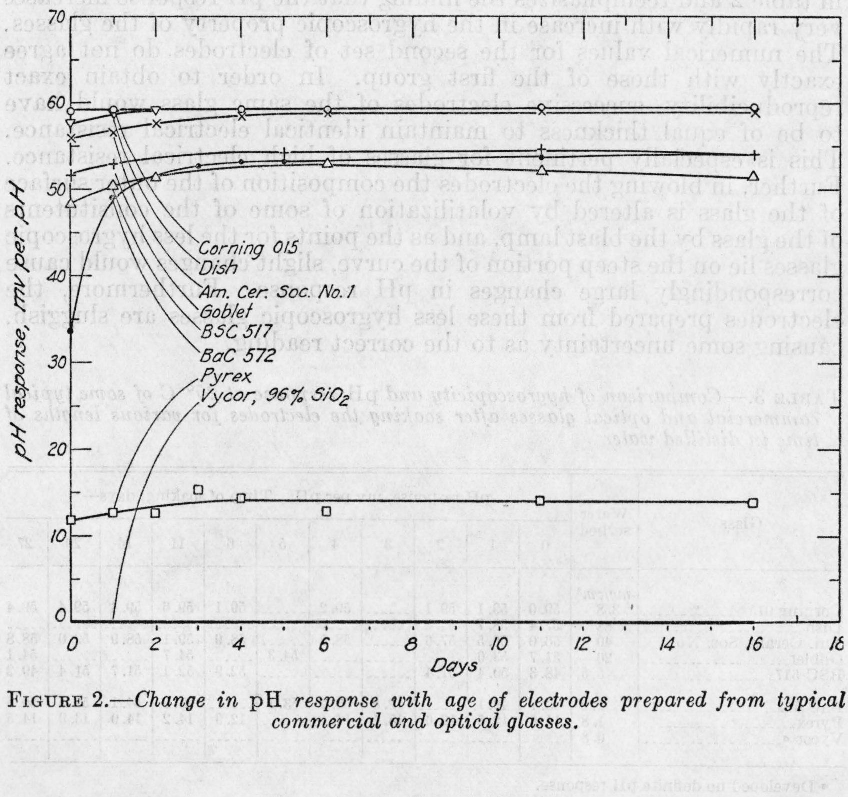

FIGURE 2.—*Change in pH response with age of electrodes prepared from typical commercial and optical glasses.*

Figure 2 indicates that electrodes prepared from all the glasses improved in their pH response during immersion in distilled water. However, they did not continue improving indefinitely until the pH response attained the theoretical value of 59 mv per pH, but arrived near some definite upper limit for each electrode by the end of the fourth day. Although most of the glasses retained their relative positions, a glass such as the BaC 572 did not do so. Undoubtedly this feature of BaC 572 is caused by a differential behavior of this glass immersed in water or dilute acids in contrast to its reversible sorption of water vapor at high humidities. A preferential solution of certain constituents of the glass must have taken place during the soaking period because the effect is essentially irreversible, as shown by the finding that upon drying at 110° C the pH response did not return to the initial low value.

That a preferential solution of certain constituents of the BaC 572 glass does take place relatively rapidly, leaving a silica-rich surface [7, 4, p. 151], is shown by the appearance of a nonreflecting film upon leaching polished surfaces in 1-percent HNO_3 at room temperature. The BaC 572 glass develops a surface film of approximately one-quarter wave length in about 24 hours, whereas periods of 2 weeks and more than 2 months are required for the BSC 517 and F 620 glasses, respectively.

2. pH RESPONSE OF GLASSES IN REGIONS OF CHANGING CHEMICAL DURABILITY

Upon determining the hydrogen electrode function of these glasses at higher pH values, the relation of pH function to the hygroscopicity was not so rigorous. For example, when the pH response of these electrodes was tested with the three buffers normally used for calibrating glass electrodes, i. e., pH values of 4.01, 6.77, and 9.15,[5] the results were erratic. These values for $\Delta E/\Delta pH$ were considerably different from those obtained in the acid buffers. This was particularly true among the optical glasses. The choice of buffers with these pH values for examining the relation of pH response to hygroscopicity is obviously undesirable as the optical glasses are known to be severely attacked in this pH range [4, p. 151], and voltage departures are known to accompany any change in chemical durability of the glass [5].

In order to emphasize the necessity for comparing the hygroscopicity with the electrode function obtained in a pH range over which the durability of the glass is constant, some voltage departures of the electrodes were ascertained over a pH range from 2 to 12. These buffers were prepared from the Britton-Robinson Universal mixture [8] used in the previous determinations of durability [4, 5]. For experimental simplicity the Beckman glass electrode was taken as the reference electrode. This tacitly assumes that the Beckman glass responds perfectly to the hydrogen-ion activity of the buffer solutions, and that all voltage anomalies observed are to be accredited to the electrodes prepared from the experimental glasses. Such an assumption is known not to be rigorously true and is only legitimate for pur-

[5] These buffers were prepared and standardized by the pH Standards Section of the National Bureau of Standards.

poses of illustration. If the reference electrode and the electrode prepared from an experimental glass had equal responses to hydrogen-ion activity, the voltage would remain constant over the entire pH range.

The results obtained by this procedure are listed in table 4. A small voltage departure for the window and blue bottle glasses is evident in the vicinity of pH 6, which becomes more pronounced beyond pH 9. This is compatible with the durability curves previously observed for similar glasses in which detectable attacks were obtained by these same buffer solutions near pH 6, with a more vigor-

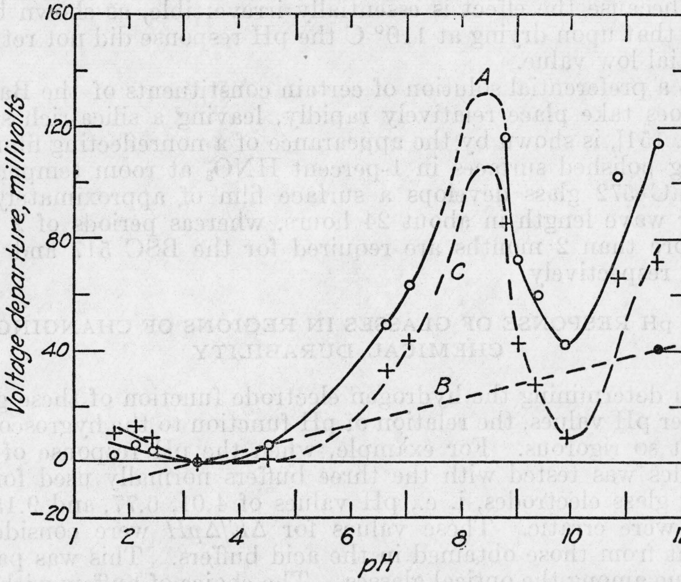

Figure 3.—*Voltage departure of an electrode prepared from BaC 572, using the Beckman glass electrode as the reference electrode.*

Total voltage departure, *A;* voltage departure imposed by low hygroscopicity, *B;* voltage departure attributable to durability of the glass and other causes, *C,* using pH 3.3 as the reference point.

ous attack beyond pH 9 [4, p. 151]. A conspicuous example of a voltage-departure curve that reflects this durability shift of the glass [4] is furnished by an electrode prepared from the BaC 572 glass, figure 3 and table 5. Upon subtracting from the total voltage departure, the departure attributable to the low hygroscopicity, 59.0−54.1=4.9 mv per pH (dashed straight line), one obtains a curve that presumably is the result of the durability shift of the glass and other causes, such as the electrode response to ions other than hydrogen [9].

The negative departures recorded in table 4 for the Corning 015 glass and the dish imply that their chemical durabilities are superior to the glass of the reference electrode in the region beyond pH11.

TABLE 4.—*Voltage departures exhibited by electrodes prepared from various glasses, using the Beckman glass electrode as reference electrode*

pH	Corning 015	Glass		Blue bottle	F 620
		Dish	Window		
	mv	*mv*	*mv*	*mv*	*mv*
1.9	0	0	0	0	0
2.3	0	1	0	0	3
3.3	0	0	0	0	12
4.3	0	0	1	0	28
5.1	1	0	0	0	39
5.9	1	−1	2	0	53
6.4	2	−1	4	1	77
6.9	2	0	6	3	90
7.3	2	3	7	4	106
8.6	1	0	13	8	130
9.5	1	−1	13	11	154
10.4	0	−1	21	22	195
11.2	−1	−11	31	37	229
11.6	−2	−22	38	47	269

TABLE 5.—*Voltage departure exhibited by an electrode prepared from BaC 572 glass, using the Beckman glass electrode as reference electrode*

pH	Total voltage departure	Voltage departure imposed by low hygroscopicity	Voltage departure attributed to attack and other causes
	mv	*mv*	*mv*
1.8	2	−7	9
2.1	6	−6	12
2.5	4	−4	8
3.3	0	0	0
4.6	6	6	0
6.6	49	16	33
7.0	63	18	45
8.8	116	27	89
9.0	72	28	44
9.4	60	30	30
9.9	42	32	10
10.8	102	37	65
11.5	114	40	74

V. CONCLUSIONS

The present work indicates that the pH response of an optical glass can furnish useful information as an indicator of serviceability, i. e., its ability to maintain a clear polished surface upon exposure to the atmosphere. In fact, it seems reasonable to expect satisfactory serviceability from any glass with a pH response of less than 57 mv per pH at 25° C in acid solution. Two of the glasses tested that failed to maintain clear surfaces, Corning 015 and the glass dish, had very high hygroscopicity values and gave pH responses close to the theoretical. Glasses of intermediate hygroscopicity exhibit only a slightly poorer response. On the other hand, the superior glasses, both optical and industrial, exhibit very poor electrode function and low hygroscopicity. This evidence furnishes strong support for, or

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is certainly compatible with, the theory that the glass electrode functions as a water electrode [10].

The voltage departures that accompany any change in chemical durability of the glass somewhat complicate the interpretation of the experimental results, but this can be largely avoided by confining the voltage observations between pH 2.0 and pH 4.

The relation between the pH response and hygroscopicity of a glass adds pertinent data toward the formulation of an acceptable theory of the glass electrode. The asymmetry potential and most or perhaps all of the conspicuous voltage departures of the glass electrode [1, 10, 11] are, at least, qualitatively rationalized [4, 5, 10, 12, 13]. There still remains the problem of ascertaining whether the voltage responses of some glasses under special conditions to ions other than hydrogen are true equilibrium responses or merely voltage departures resulting from changes in chemical durability of the glasses under the imposed conditions.

The hygroscopicity data might readily eliminate the condenser theory of the glass electrode [3] as it seems unlikely that the more hygroscopic the glass the better would be the condenser and hence the better the electrode function.

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