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Corresponding Member of the Academy of Sciences of the USSR B. P. NIKOLSKY, M. M. SHULTS,

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Abstract

Full Text

Physical Chemistry

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N. V. PESHEKHONOVA, and A. A. BELOUSTIN

FEATURES OF THE ELECTRODE BEHAVIOR OF GLASSES CONTAINING TWO ACIDIC (GLASS-FORMING) OXIDES

In work (1) it was shown that the electrode behavior of glasses containing two acidic oxides (for example, silica and boric anhydride) depends on the distribution in the glass of basic oxides between the acidic ones.

Glass electrodes made of binary alkali-silicate glasses, i.e., containing only one acidic oxide—SiO_2—as well as of alkali glasses containing oxides of a basic character (modifiers)—oxides of cesium, calcium, barium, lanthanum, etc.—possess a hydrogen function over a wide pH interval ([2],[3])

$$\varphi = \varphi^\circ + \vartheta \lg a_{H^+} \quad \left(\vartheta = \frac{RT}{F} \cdot 2.303\right), \tag{1}$$

to which the rectilinear segment aa of curve 1 in Fig. 1 corresponds. As a result of the process of ion exchange between the glass and the solution, proceeding according to the equation

$$H^+\,(\text{glass}) + M^+\,(\text{solution}) \rightleftarrows H^+\,(\text{solution}) + M^+\,(\text{glass}) \tag{2}$$

at certain pH values there occurs a transition from the hydrogen to the metallic function of the glass electrode ([4]-[7]) (segment $a'''b'_b$ of curve 1 in Fig. 1). According to the ion-exchange theory of the glass electrode ([4]), curve 1 is described by the equation

$$\varphi = \varphi^0 + \vartheta \lg\left(a_{H^+} + K a_{M^+}\right), \tag{3}$$

where K is the equilibrium constant of process (2).

However, in experiment, in the transition region $a'''b'$ some deviations from equation (3) are observed, which increase upon introduction into the glass of a second acidic oxide, for example B_2O_3 (curve 2 in Fig. 1). This can be explained

Fig. 1. Schematic representation of the electrode behavior of glasses of various types: 1 —binary alkali-silicate glasses and glasses containing ions—modifiers; 2 —complex glasses containing glass-forming and modifying components; 3 —simple glasses with small amounts of a second glass-former; 4 —glasses containing relatively large amounts of a second glass-former. The dashed portions of curves 1, 2 correspond to equation (3)

Figure 1: Fig. 1. Schematic representation of the electrode behavior of glasses of various types: 1 —binary alkali-silicate glasses and glasses containing ions—modifiers; 2 —complex glasses containing glass-forming and modifying components; 3 —simple glasses with small amounts of a second glass-former; 4 —glasses containing relatively large amounts of a second glass-former. The dashed portions of curves 1, 2 correspond to equation (3)

by the presence in the glass of hydrogen ions with different strengths of bonding to the glass (^{5}-^{7}). If a sufficiently large quantity of boron or aluminum oxides is introduced into the glass, one can obtain a glass electrode with a metallic function over a wide pH region (^{9}-^{11}) (curve 4 in Fig. 1).

It may be considered that glasses containing no boron or aluminum behave like a weak acid ($K \sim 10^{-12}$, curve 1), whereas the introduction of boron and aluminum leads to the formation in the glass of stronger alumino- or borosilicic acids ($K \sim 10^{-12}$; $K \to 1$ for curve 4), where the hydrogen ion is bound relatively more weakly (^{12}). Curves of types 2 and 4 are characteristic of complex glasses, for example of glasses belonging to the system Na_2O–CaO–SiO_2 with additions of Al_2O_3, B_2O_3, ZrO_2, and other glass-forming oxides (^{13},^{14}).

The generalized theory of the glass electrode (^{8}) also predicted the possibility of the existence of curves of type 3 (Fig. 1), where segment aa' corresponds to the hydrogen function of the glass, caused by hydrogen ions bound with the anions of both strong and weak acids in the glass phase; segment $a'b'''b''$ corresponds to the transition region from the hydrogen to the metallic function, corresponding to replacement by alkali-metal ions of hydrogen ions, weakly bound to the glass anions. In segment $b''d$, the hydrogen function is manifested (in part), due to more strongly bound hydrogen ions, which are displaced by alkali-metal ions at higher pH values (transition to the region $d'b'''$, corresponding to the complete metallic function).

Experimentally, for the first time it proved possible to detect such a differentiation of the electrode properties of glass into properties dependent on strongly acidic and weakly acidic groups in glasses of the ternary system Li_2O—Al_2O_3—SiO_2 in the region of low alumina content (from 0 to 3 mol.%).

Fig. 1. Schematic representation of the electrode behavior of glasses of various types: 1 —binary alkali-silicate glasses and glasses containing ions—modifiers; 2 —complex glasses containing glass-forming and modifying components; 3 —simple glasses with small amounts of a second glass-former; 4 —glasses containing

relatively large amounts of a second glass-former. The dashed portions of curves 1, 2 correspond to equation (3).

Figure 2 presents the dependence of the e.m.f. of a glass-calomel cell on the pH of a buffer solution with a constant lithium content ($3N$). The pH value was measured with a hydrogen-calomel cell. The measurements were carried out at room temperature*. In conducting the experiments, we changed the pH, as a rule, in the direction of increase. When the pH was changed in the reverse direction, the shape of the curves was reproduced sufficiently well; a small hysteresis was observed only in the transition region (the dashed line with arrows).

Figure 3 shows the electrode behavior of glasses of the system Na_2O—B_2O_3—SiO_2. Curves are given here for two concentrations of sodium ion in solution: $0.1N$ and $3N$. From Fig. 3 it is evident that boric oxide produces a differentiating effect analogous in character to the effect of alumina. The relative positions of the curves for different sodium concentrations in solution confirm the interpretation given above of the individual portions of curves of type 3 in Fig. 1. Indeed, as is seen from Fig. 3, the vertical distance between the portions of the sodium function of the curves for glasses with 6.6 and 9.4 mol.% B_2O_3 is close to the theoretical value, equal to

$$\Delta E = \vartheta \lg \frac{a'_{\mathrm{NaCl}}}{a_{\mathrm{NaCl}}} =$$

= 83 mV. Similar curves were obtained by us on other glasses of these same systems, differing in lower or higher contents of lithium oxide (from 24 to 33 mol.%) or sodium oxide (from 16 to 25 mol.%), and also on glasses of other systems, including two acidic (glass-forming) oxides:

$$\mathrm{Li_2O—R_{nO}m—SiO_2} \qquad (\mathrm{R_{nO}m = B_2O_3,\ Ga_2O_3,\ ZnO_2}) \qquad \text{(I)}$$

$$\mathrm{Na_2O—R_{nO}m—SiO_2} \qquad (\mathrm{R_{nO}m = Al_2O_3,\ Ga_2O_3,\ Fe_2O_3,\ GeO_2,\ SnO_2,\ TiO_2,\ ZrO_2,} \qquad \text{(II)}$$

$$\mathrm{P_2O_5,\ Sb_2O_3,\ Bi_2O_3}).$$

The degree of differentiating influence of different oxides, which appears at low contents of them, is different. For most of these oxides it is also characteristic that relatively large additions of them (for Al_2O_3, Fe_2O_3, B_2O_3, ZrO_2 this is 3-9%) lead to the disappearance of the second hydrogen region in the pH interval studied, from 0 to 14, caused by the presence in the glass of a weaker acid, as a result of which curves of type 4 in Fig. 1 are obtained. Apparently, these phenomena are directly related to the representa–

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Fig. 2. Dependence of the potential of the glass electrode on pH ($C_{\mathrm{Li}^+} = 3\,N$) for glasses of composition 27% Li_2O –X% Al_2O_3 –$(73 - X)$% SiO_2 (mol.%).

Figure 2: Fig. 2. Dependence of the potential of the glass electrode on pH ($C_{\mathrm{Li}^+} = 3\,N$) for glasses of composition 27% Li_2O –X% Al_2O_3 –$(73 - X)$% SiO_2 (mol.%).

Fig. 3. Dependence of the potential of the glass electrode on pH for glasses of composition 22% Na_2O –X% B_2O_3 –$(78 - X)$% SiO_2 (mol.%). A – $C_{\mathrm{Na}^+} = 0.1\,N$; B –$C_{\mathrm{Na}^+} = 3.0\,N$.

Figure 3: Fig. 3. Dependence of the potential of the glass electrode on pH for glasses of composition 22% Na_2O –X% B_2O_3 –$(78 - X)$% SiO_2 (mol.%). A – $C_{\mathrm{Na}^+} = 0.1\,N$; B –$C_{\mathrm{Na}^+} = 3.0\,N$.

* The curves in Figs. 2 and 3 are artificially shifted along the ordinate.

···the notion that alkali metals in complex silicate systems are bound primarily with such oxides as Al_2O_3, B_2O_3, etc. ([15–17]).

Thus, the "differentiating effect" we have found for the second acidic oxide at low content in glasses that are simple in composition is common to all glass-forming oxides. This effect clearly confirms the basic propositions of the generalized theory of the glass electrode and is in agreement with modern ideas about the bonding and coordination of atoms of glass-forming elements in glass ([18,19]).

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CITED LITERATURE

1. B. P. Nikol' skii, N. P. Isakova, M. M. Shul' ts, DAN (1961) (in press).
2. D. A. MacInnes, D. Belcher, *J. Am. Chem. Soc.*, **53**, 3315 (1931).
3. G. A. Perley, *Anal. Chem.*, **21**, 341, 394, 559 (1949).
4. B. P. Nikol' skii, *ZhFKh*, **10**, 495 (1937).

5. B. P. Nikol' skii, T. A. Tolmacheva, *ZhFKh*, **10**, 513 (1937).
6. M. M. Shul' ts, *Uch. zap. LGU*, ser. chem., no. 13, 169 (1953).
7. B. P. Nikol'skii, M. M. Shul'ts, N. V. Peshekhonova, *ZhFKh*, **32**, 20 (1958).
8. B. P. Nikol' skii, *ZhFKh*, **27**, 724 (1953).
9. B. Lengyel, E. Blum, *Trans. Farad. Soc.*, **30**, 461 (1934).
10. M. M. Shul' ts, L. G. Aio, *Vestn. LGU*, no. 8, 153 (1955).
11. G. Eisenmann, D. O. Rudin, J. U. Casby, *Sci.*, **126**, 831 (1957).
12. L. Pauling, *The Nature of the Chemical Bond*, Moscow, 1947, p. 382.
13. B. P. Nikol' skii, T. A. Tolmacheva, *ZhFKh*, **10**, 504 (1937).
14. B. Lengyel, B. Csákvári, *Acta Chim. Acad. Sci. Hung.*, **25**, 369 (1960).
15. R. L. Müller, *ZhTF*, **25**, 236 (1955).
16. A. A. Appen, *ZhPKh*, **26**, 569 (1953); **27**, 121 (1954).
17. B. P. Nikol' skii, M. M. Shul' ts, *The Glassy State*, Publishing House of the Academy of Sciences of the USSR, 1960, p. 292.
18. M. M. Shul' ts, *Vestn. LGU*, no. 22, 40 (1960).
19. *The Glassy State*, Publishing House of the Academy of Sciences of the USSR, 1960.

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