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Bifunctional Electrode Glasses of Sodium-potassium Function

Dwufunkcyjne szkła elektrodowe o funkcji sodowo-potasowej

Бифункциональное электродное стекло с натриево-кальцеевой функцией

The selectivity of electrodes made of sodium-alluminium silica glasses, indicating sodium or potassium function, depends essentially only on the ratio Na_2O / Al_2O_3 or Na^+ / Al^{3+} in the glass. This dependence is expressed by Eisenman's equation [1, 2] :

$$\log K^{pot}_{NaK} = 7{,}42 \log (Na^+ / Al^{3+}) - 3{,}2 \quad (1)$$

The larger ratio Na^+/Al^{3+}, the lower affinity of the glass to Na^+ is in relation to K^+. In all alluminium silica glasses in which the ratio of Na^+/Al^{3+} is higher than 1 and the higher value it has, the lower strength of anion field is as a result of shielding.

In extreme cases, the ratio Na^+/Al^{3+} does not decide of selectivity change Na^+ to K^+ and so:

- when the ratio Na^+/Al^{3+} is lower than 1, so the excess of atoms of Al does not participate in tetrahedral coordination and does not make $(AlOSi)^-$ sites intensity which is necessary to get the selectivity in relation to cations,

- when the ratio Na^+/Al^{3+} is very high, the glass becomes more increasingly hydrated, what causes the decrease of selectivity.

Considering the selectivity of glass electrodes, one should mention that it is not important if Na^+, Al^{3+}, Si^{4+} "per se" are present in the glass. Na_2O might be replaced by another oxide (M_2O) f.ex.: Li_2O, K_2O, Rb_2O, Cs_2O. Glasses of same ratio $M^+/x\ Al^{3+}$ can be characterized by similar selectivities and the equation 1 can be noted in a generalized form:

$$\log K_{NaK}^{pot} = 7,42 \log (M/Al) - 7,42 \log x - 3,2 \qquad (2)$$

where x has values: for Li = 2,5
for K = 0,6
for Rb = 0,5
for Cs = 0,37.

The present paper describes results of investigations on lithium-alluminium and sodium-alluminium silica glasses from the point of view of obtention of electrodes of selectivity coefficient NaK = 1, i.e. sodium - potassium function. Such a glass as this one, would be adequate to carry out simple and quick estimations of sodium and potassium in pure solutions, their sum and also indirect estimation of potassium in the presence of sodium. The amount of alkali metals' sum ($Na^+ + K^+$) is often used as a purity indicator of many reagents, in water analysis. It has also meaning in biological analysis and the like [3,4] .

Electrode properties of bifunctional glass are also interesting from the theoretical point of view.

EXPERIMENTAL

There were investigated electrodes made of lithium-alluminium and sodium-alluminium glasses with the admixture of TiO_2 of composition shown in tab. 1

Tab. 1. The composition of electrode glasses expressed in % m

Glass nr	Li_2O	Na_2O	Al_2O	TiO_2	SiO_2	M^+/Al^{3+}
1	21		3	4	71	7
2	28		4	4	63	7
3	24		3	5	68	8
4		21	7	5	67	3
5		24	8	5	63	4

The glasses were prepared from the appropriate oxide sets. They were smelted in the platinium + 5% Au crucible in a specially constructed furnace. The furnace temperature was gradually raised till 1350°C, then the glass mass was stayed for a few hours until it became homogeneous and clear. From so prepared glass, bulb electrode membranes were formed. Selected electrodes were filled with electrode solution, there were drawn out reference electrodes Ag/AgCl and conditioned in water for about 14 days [5]. It was examined the resistance according to [6] and tested. Testing included the basic characteristics in water solutions NaCl and KCl of concentration 10^{-1} - 10^{-5} M/dm^3 (the solutions were buffered by "tris" to pH 10) [7,8].

Obtained results were illustrated on figures 1-5.

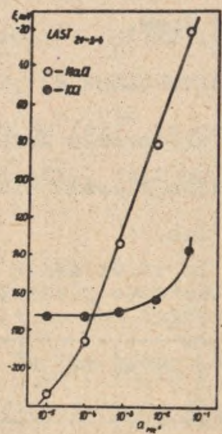

Fig. 1. Dependence of the logarithm of the rate constant of acetanilide bromination on pH. T = 298 K; μ = 1,05; [Br$^-$] = 1-0.045, 2 - 0.100, 3 - 0.182, 4 - 0.363 mol l^{-1}

Dependence Emf / mV of cell: glass electrode - reference electrode on the activity of metals'ions Na^+, K^+ . (Reference electrode Orion 90-02-00).

The most encouraging results were obtained for $NAST_{21-7-5}$ glass. This glass is characterized by linear course of sodium and potassium characteristics in range from 10^{-1} to 10^{-3} M/dm^3. The characteristics slopes are 55 mV/pNa and 45 mV/pK respectively.

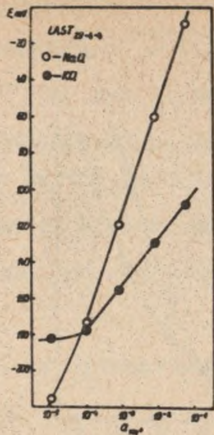

Fig. 2. Dependence of the rate constant of acetanilide bromination on the squared level of histidine concentration. $[Br^-]$ = 0.182, μ = 1.05; T = 298 K; pH = 1 - 3.0, 2 - 3,6, 3 - 3.7, 4 - 3.9, 5 - 4.4

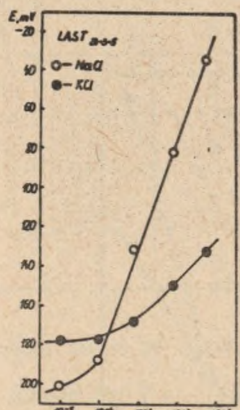

Fig. 3. Dependence of the rate constant of acetanilide bromination in the presence of histidine on pH. $[Br^-]$ = 0.182; = 1.05; T = 298 K; [histidine] = 1 - 0., 2 - 4.6 10^{-4}, 3 - 7,9 10^{-4}, 4 - 12.0 10^{-4}, 5 - 14.3 10^{-4}, 6 - 17.1 10^{-4} mol l^{-1}

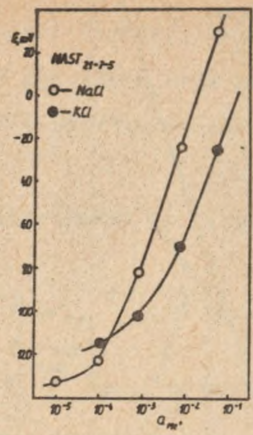

Fig. 4. Dependence of the value of the increase in the rate constant of acetanilide bromination on histidine concentration. $[Br^-]$ = 0.182; μ = 1.05; T = 298 K; pH = 1 - 3.0, 2 - 3.6, 3 - 3.7, 4 - 3.9, 5 - 4.4

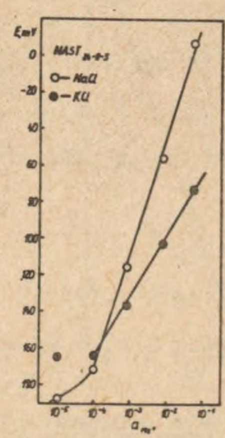

Fig. 5. Intervals of the existence of histidine forms at varying degrees of protonation depending on the pH of the solution

It was stated that this glass makes is possible to estimate potassium ions in the absence of sodium ions in the range of concentration 10^{-1} - 10^{-3} M, and in the range of 10^{0} - 10^{-2} the course of basic characteristics is a straight line.

In order to obtain better results there were undertaken attemps of getting glass of higher selectivity in relation to potassium. There were smelted electrode glasses of composition shown in tab. 2.

Tab. 2. The composition of bifunctional electrode glasses expressed in % m

Glass nr	Na_2O	Li_2O	Al_2O_3	TiO_2	SiO_2	M^+/Al^{3+}	Na_2O + Al_2O_3
1	15	-	3	5	77	5	18
2	20	-	4	5	71	5	24
3	25	-	5	5	65	5	30
4	-	20	2	5	73	10	22
5	-	30	3	5	62	10	33
6	20	-	2	5	73	10	22
7	30	-	3	5	62	10	33

The electrodes were made of glasses of composition shown in tab. 2 (except of glass nr 3). The electrodes were tested in solutions NaCl and KCl above mentioned. After series of elementary examinations of electrodes made of above mentioned glasses, it was stated that encouraging results were obtained for the electrodes made of $NAST_{15-3-5}$ glass. The electrodes were tested both in pure solutions of NaCl and KCl and as well in mixed solutions containing sodium and potassium of total concentration from 10^{-1} to 10^{-4} M/dm^3 and of composition shown in tab. 3.

Tab. 3. Dependence Emf of cell: glass electrode $NAST_{15-3-5}$ - reference electrode - on Na^+ and K^+ ions' activity in solutions

Quantitative composition of solution in moles		E (mV) cell:-glass electrode $NAST_{15-3-5}$ - reference electrode		
KCl	NaCl	A	B	C
0,1	-	107	105	104
$7,5\cdot10^{-2}$	$2,5\cdot10^{-2}$	108	112	112
$5\cdot10^{-2}$	$5\cdot10^{-2}$	110	115	115
$1\cdot10^{-2}$	$9\cdot10^{-2}$	115	118	120
-	10^{-1}	118	118	120
10^{-2}	-	66	68	65
$7,5\cdot10^{-3}$	$2,5\cdot10^{-3}$	69	68	68
$5\cdot10^{-3}$	$5\cdot10^{-3}$	68	70	70
$1\cdot10^{-3}$	$9\cdot10^{-3}$	68	71	70
-	10^{-2}	68	72	71
10^{-3}	-	24	28	28
$7,5\cdot10^{-4}$	$2,5\cdot10^{-4}$	26	32	27
$5\cdot10^{-4}$	$5\cdot10^{-4}$	25	29	26
$2,5\cdot10^{-4}$	$7,5\cdot10^{-4}$	24	28	26
-	10^{-3}	18	25	18
10^{-4}	-	15	8	9
-	10^{-4}	25	19	30

The course of basic characteristics for bifunctional electrodes made of $NAST_{15-3-5}$ glass was illustrated in fig. 6.

Dependence Emf (mV) of cell: - glass electrode $NAST_{15-3-5}$ - reference electrode - on Na^+ and K^+ ions', activity.

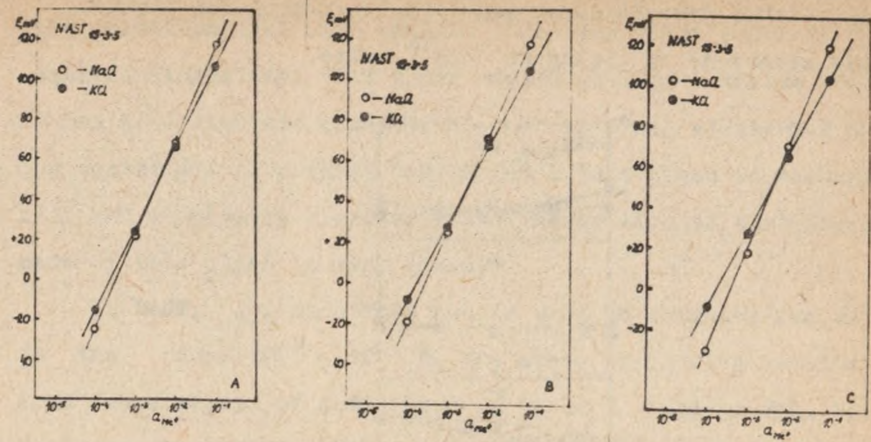

Fig. 6. Dependence of the constant k_c on pH

Tab. 4. Selectivity coefficients of glasses

Glass Nr	Na/Al	Li/Al	K^{pot}_{NaK} measured	K^{pot}_{NaK} calculated
1_I		7	0,0025	1,38
2_I		7	0,0038	1,38
3_I		8	0,0014	39,3
4_I	3		0,14	1,94
5_I	4		0,073	17,90
1_{II}	5		~1	97,95
2_{II}	5		0,502	97,95
3_{II}	5		-	97,95
4_{II}		10	0,00871	21,38
5_{II}		10	0,00851	21,38
6_{II}	10		0,00871	16600
7_{II}	10		0,00631	16600

On the basis of these above results illustrated in table 3 there were drawn curves visible in fig. 7.

In the tab. 4 the values selectivity coefficients are summarized. The coefficients were determined by the separate solution method and calculated from Eisenman equation for sodium and lithium glasses according to rising Me^{1+}/Al^{3+} ratio.

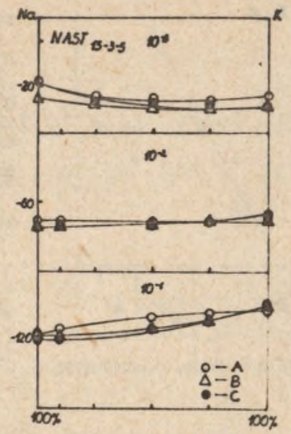

Fig. 7. Dependence of the logarithm of histidine catalytic constant on pH

DISCUSSION

1. In papers [9-12] it was shown that the addition of TiO_2 improved physical and chemical properties of sodium and lithium electrode glasses. Addition of TiO_2 was also used in obtaining bifunctional sodium-potassium glasses. In the selective glass towards cations of alkali metals there are present groups $(Al-O-Si)^-$, the introduction of quadrivalent element f, ex. Ti, into the glass, makes it possible to form $(TiO_6Si)^{-2}$ groups which, also the selectivity of glasses towards alkali cations is observed.

2. The best bifunctional glass which has been obtained so far, is the glass of composition Na_2O - 15, Al_2O_3 - 3, TiO_2 - 5, SiO_2 - 77 ($NAST_{15-3-5}$). This glass has respectively

long formation area what enables obtaining glass bulbs of required dimensions. This glass smelts well with sodium one. It has good electric conductivity and obtained electrodes have low resistance of several dozens MΩ . This glass is mechanically and chemically resistant. The answer time of electrodes made of this glass is very short.

3. $NAST_{15-3-5}$ electrode can be used to estimate sum $Na^{+} + K^{+}$ in the range $10^{-1} - 10^{-4}$ M. The above conclusion results from the analysis of data shown in Table 3 and on Fig. 7. Replacement of the solution containing Na^{+} ions by the solution containing K^{+} ions of the same activity, causes insignificant change Emf of the above mentioned cell.

Practically, we get the most insignificant change of Emf at the point of intersection of straight lines corresponding to sodium and potassium characteristics i.e. for concentration $1 \cdot 10^{-3}$ M.

4. For the electrodes made of glasses which have the composition shown in table 1,2 there were determinated selectivity coefficients using separated solution methods [13] and by Eisenman's equations (1) (Tab. 4). These selectivity coefficients do not show concidence. Eisenman's equation can not be used to glasses having been investigated. Moreover, one should mention that selectivity coefficient has the most rational meaning for the electrodes of which characteristics are straight parallel lines. However, when the lines intersect each other, or one of them is not a straight line the accounting of selectivity coefficient is aimless because, for this case, value of selectivity coefficient in every area of concentration is different.

5. $NAST_{15-3-5}$ electrodes were used to estimate sodium and potassium sums and to estimate potassium in different salts and oxides of elements of rare earths with positive results.

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STRESZCZENIE

Otrzymano szkło dwufunkcyjne o funkcji sodowo-potasowej. Szkło o składzie Na_2O - 15; Al_2O_3 - 3; TiO_2 - 5; SiO_2 - 77 charakteryzuje długi obszar formowania, łatwo stapia się ze szkłem sodowym, posiada dobre przewodnictwo elektryczne i jest

wytrzymałe mechanicznie i chemicznie. Elektrody otrzymane z ww. szkła mają charakterystykę nernstowską w zakresie 10^{-1} - 10^{-5} M i mogą być stosowane do oznaczeń sumy sodu i potasu oraz do pośrednich oznaczeń potasu w obecności sodu.

РЕЗЮМЕ

Получено бифункциональное стекло с натриево-калиевой функцией. Стекло состава Na_2O-15; Al_2O_3-3; TiO_2-5; SiO_2-77 характеризуется длинной зоной формирования, оно легко сплавляется с натриевым стеклом, обладает хорошей электрической проводимостью, большой механической прочностью и химической устойчивостью.

Электроды из вышеупомянутого стекла обладают нернстовской характеристикой в области 10^{-1}- 10^{-5} М и могут быть использованы для определения суммы натрия и калия, я также для определения калия в присутствии натрия.