ANNALES
UNIVERSITATIS MARIAE CURIE-SKŁODOWSKA
LUBLIN — POLONIA
VOL. XXXIII, 1 SECTIO AA 1978

Instytut Chemii UMCS
Zakład Chemii Analitycznej i Analizy Instrumentalnej

Kazimierz SYKUT, Jadwiga DUMKIEWICZ,
Ryszard DUMKIEWICZ

Ion-Selective BMSA Electrodes with Pseudo-Liquid Potential-Determining Phase

Elektrody jonoselektywne typu BMSA z pseudociekłą fazą potencjałotwórczą

Ионоселективные электроды с псевдожидкой мембраной

INTRODUCTION

One of the types of ion-selective electrodes are electrodes with a liquid membrane whose construction design must include a reservoir with an internal aqueous solution containing a reference electrode with a stable potential, a reservoir of liquid exchanger, and a contact in the form of a neutral porous membrane. The liquid exchanger should saturate the membrane and be in contact with the internal solution [1-6]. The properties of the electrode depend to a large extent on the electroactive substance used. An important role is also played by the design of the construction. Well-functioning electrodes now on sale have a fairly complicated structure consisting of 15-20 construction elements.

Even the best types of electrodes with a liquid membrane have their disadvantages. Major ones among them are: the necessity of periodic replacement of the membrane and the internal solutions as well as the instability of standard potential. Attempts at simplifying the construction of electrode by exclusion of the reservoir of the solution of liquid exchanger [7, 8] and by constructing electrodes in which the reference electrode was covered with a membrane layer containing liquid exchanger [9, 10] have failed to produce satisfactory results.

Despite the inconveniences mentioned above, electrodes with the liquid membrane are produced in batches because, with a good construction design, one obtains by exchanging the filling of the electrode, a number of electrodes selective for particular ions.

The basic object of our research was the construction of ion selective electrodes which would come up to the standard set up for electrodes with liquid membrane and which would combine all their virtues with the simplest possible design. This aim was achieved when the electrode called BMSA* [11, 12] was constructed by us. It contained gelled plasticizer PVC as the carrier of potential-determining (D.P.) phase and a reference electrode. The construction design, which made possible the use of deeply modified PVC, permitted us to obtain a good complex of parameters of the electrode which could not be obtained by those researchers who used the coated-wire construction [9, 10].

EXPERIMENTAL PART

The construction of BMSA electrodes

BMSA electrode (Fig. 1) consists of exchangeable sensor "g" in which there is an active factor immobilized in base (potential-

*The letters BMSA in the name of the electrode present the composition of the potential-determining phase:

Basis (B)	- polymer, e.g. PVC
Modifier (M)	- plasticizers
Active substance (SA)	- ion-exchangers

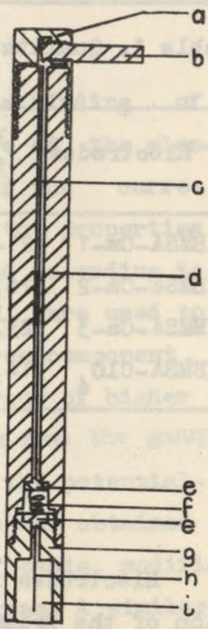

Fig. 1. Design of BMSA electrode; a - nut, b - pin, c - connecting wire, d - body of the electrode, e - contacting elements, f - contacting spring, g - sensor, h - reference electrode, i - potential-determining phase

-determining phase) "i". To this phase is introduced reference electrode Ag/AgCl "h". Sensor "g" is screwed into the body of electrode "d".

Preparation of potential-determining phase and preparing electrodes

In the preparation of the potential-determining phase of BMSA electrodes appropriate quantities of polimer, plasticizer and active substance were weighed. The components were homogenized and then the air was removed from the mixture. The mixture was poured into the teflon reservoir of the electrode and gelled in the temperature of 80-150°C (depending on the composition of the D.P., the kind of polymer and plasticizer) for 15 minutes. The composition of the potential-determining phase of some electrodes is given in an attached table (Table 1). The next stage was the assembling of the electrode which consisted in screwing the sensor into body of the electrode.

Table 1. Qualitative and quantitative composition of D.P. of BMSA electrodes

Electrodes	B %	M %				SA %
		TBP	DBF	DOP	DBS	
BMSA-Ca-1	21-2	31,8	-	38,0	-	9,0
BMSA-Ca-2	16,0	25,0	25,0	-	25,0	9,0
BMSA-Ca-3	23,8	71,4	-	-	-	4,8
BMSA-ClO_4	14,5	-	72,5	-	-	13,0

Methodology of measurements

Electrodes require preliminary conditioning in 0.1 M solution of the primary ion for 12 hours. Electrodes thus prepared are stored in dry state. Before measurements are taken the electrodes require additional brief 10-15 minutes conditioning.

The electrodes were tested in solutions of the primary ion and of the interfering ion. When calibrating curves were drawn the scale of ion activity was used. Ion activity was calculated on the basis of the Debye-Huckel equation. The electromotive force of cell ISE (outside solution) SCE was measured with precision up to 1 mV.

The resistance of electrodes was measured by the method consisting in determining the time of the charging of condenser to fixed voltage of the current passing through the examined electrode [14]. The selectivity coefficient was determined by the relationship:

$$\lg K_{ij} = \pm \frac{zF\left(E_2 - E_1\right)}{2,303\ RT} - \left(\frac{z}{y}\right) \lg a_i$$

The above method has been used by many authors.

RESULTS AND DISCUSSION

Carrying out investigation which aimed at the finding of optimal composition of potential-determining phase of the electrode was accompanied by systematic observation of the correlation between the composition of this phase and the properties of the electrodes. The investigation was conducted according to diagrams 1 and 2. In diagram 1 symbols M_1, M_2, M_3 were used to mark the modifiers respectively one-, two and three-component. Symbols A_1, B_1 mark active substances from the group of higher fatty acids and symbols A_2, B_2 - active substances from the group of phosphoroorganic acids. The composition of the potential-determining phase of cation-selective electrodes was obtained by means of an appropriate choice of the kinds of basis, modificators and active substances as shown in the diagram. A similar procedure was followed in the case of anion-selective electrodes, where the components of the potential-determining phase were selected according to diagram 2.

It was found during the investigation that a good I.S. electrode can be obtained only by successive optimalization of the composition of potential-determining phase. In order to obtain a well-functioning electrode it was sometimes necessary to examine as many as several hundred different combinations of basis-modifier-active substances.

It must be emphasized that only an optimal qualitative and quantitative choice of potential-determining phase results in obtaining electrodes with characteristics approximating those of the Nerstian type. When optimalizing the composition of the potential-determining phase of the electrodes one ought to remember that apart from their proper, potential-determining function, there must also be preserved another - and no less important - factor determining the durability of the electrodes, i.e. the physical properties of the given plasticizer.

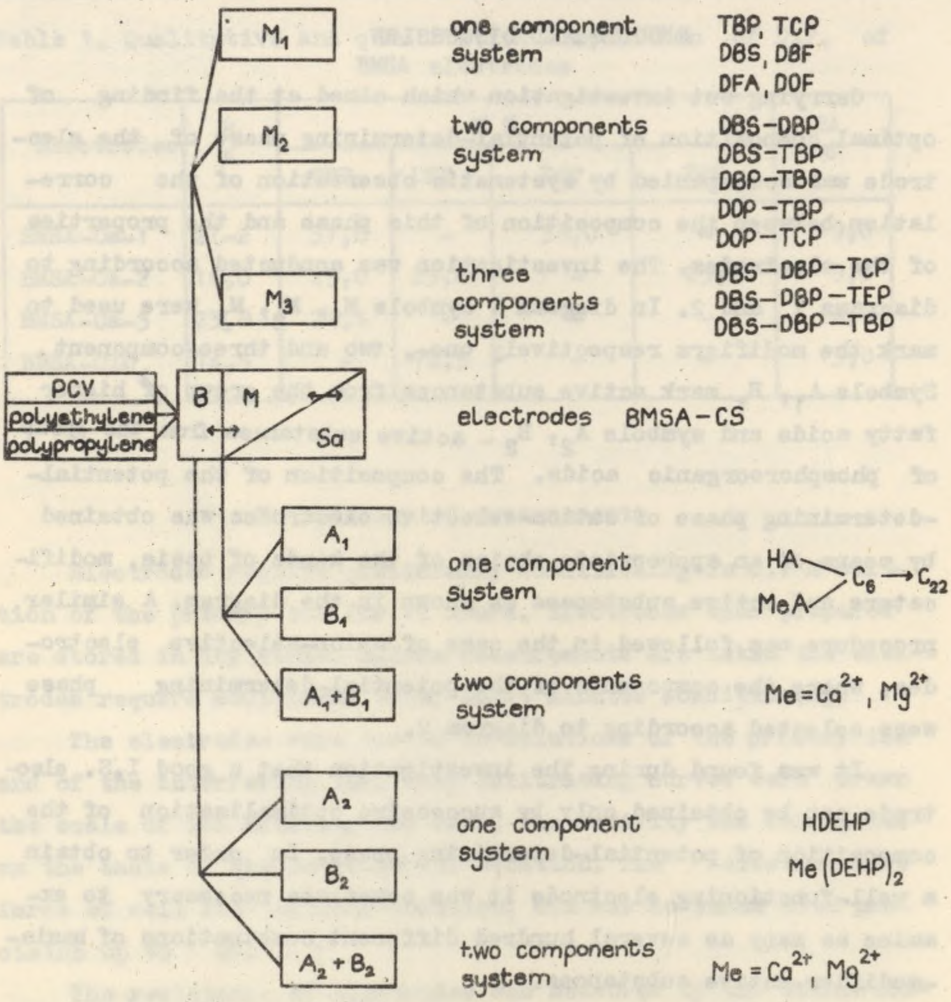

Diagram 1. Diagram of investigation on influence of composition of potential-determining phase of cation-selective electrodes on analytic parametres of these electrodes

A_1 - fatty acids F.A.
B_1 - calcium salts of fatty acids S-F.A.
A_2 - HDEHP
B_2 - Me $DEHP_2$
Me = Ca^{2+}, Mg^{2+}
M_1 - one-component plasticizer
M_2 - two-component plasticizer
M_3 - three-component plasticizer
TBP - tri-butyl phosphate
TCP - tricresyl phosphate
TCP - tricresyl phosphate
DBS - tibutyl sebacate
DBP - dibutyl phtalate
DEA - diethyl adipate
DOP - dioctyl phtalate

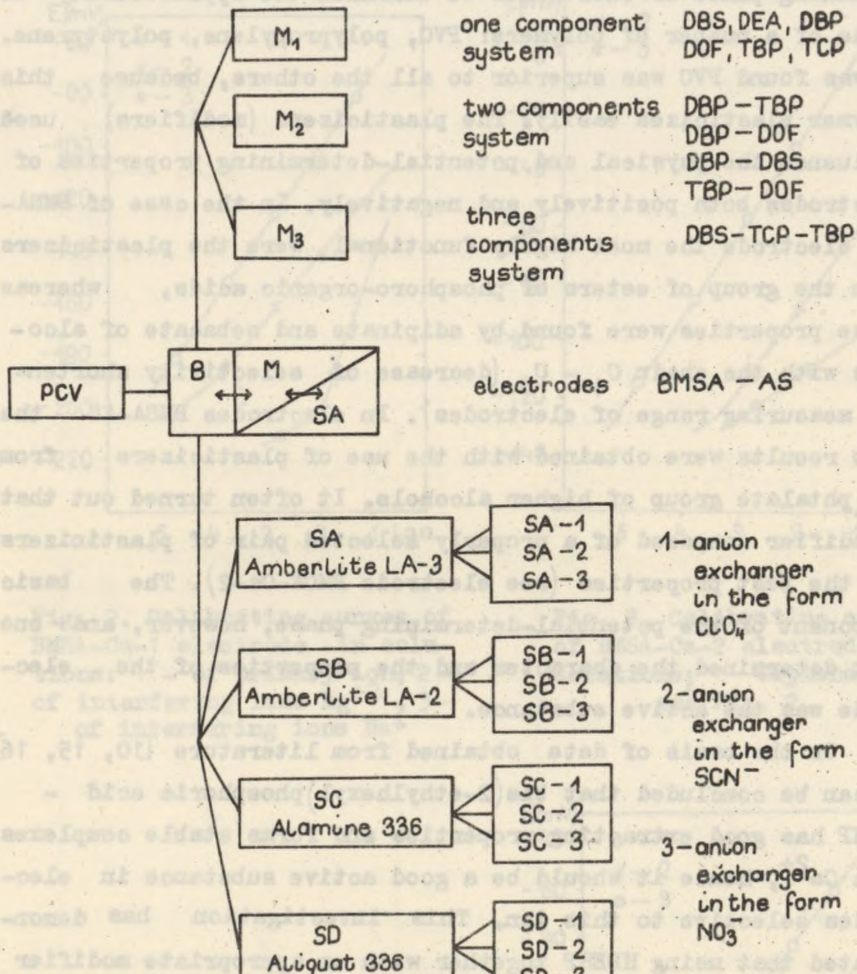

Diagram 2. Diagram of investigation on composition of potential-determining phase of anion selective electrode on analytic parameters of these electrodes

SA – active substances from group of multiparticular aliphatic amines

M_1 – one-component plasticizer

M_2 – two-component plasticizer

M_3 – three-component plasticizer

TBP – tri-butyl phosphate

TCP – tricresyl phosphate

DBS – dibutyl sebacate

DBP – dibutyl phtalate

DEA – diethyl adipate

DOP – dioctyl phtalate

In order to find the best composition of the potential-determining phase of electrodes we examined the applicability as basis of a number of polymers: PVC, polypropylene, polystyrene. It was found PVC was superior to all the others, because this polymer plasticizes easily. The plasticizers (modifiers) used influence the physical and potential-determining properties of electrodes both positively and negatively. In the case of BMSA--CS electrode the most highly functional were the plasticizers from the group of esters of phosphoro-organic acids, whereas worse properties were found by adipinate and sebacate of alcohols with the chain $C_4 - C_8$ (decrease of selectivity shortening measuring range of electrodes). In electrodes BMSA-AS the best results were obtained with the use of plasticizers from the phtalate group of higher alcohols. It often turned out that a modifier composed of a properly selected pair of plasticizers had the best properties (see electrode BMCA-Ca-2). The basic component of the potential-determining phase, however, and one that determined the character and the properties of the electrode was the active substance.

On the basis of data obtained from literature [10, 15, 16] in can be concluded that bis(2-ethylhexyl)phosphoric acid - HDEHP has good extracting properties and forms stable complexes with Ca^{2+}, hence it should be a good active substance in electrodes selective to this ion. This investigation has demonstrated that using HDEHP together with an appropriate modifier one can obtain good calcium electrodes. Figs. 2, 3 show calibrating curves of ion-selective calcium electrodes.

Fatty acids and their salts have been rarely used as active substance in ion-selective electrodes [17, 16]. Botre et al. [18] investigated the possibility of using gel of potassium stearate as exchanger in calcium electrodes without obtaining satisfactory results.

Considering extracting properties of fatty Ca^{2+} ions acids respecting to effectiveness we decided to investigate the possi-

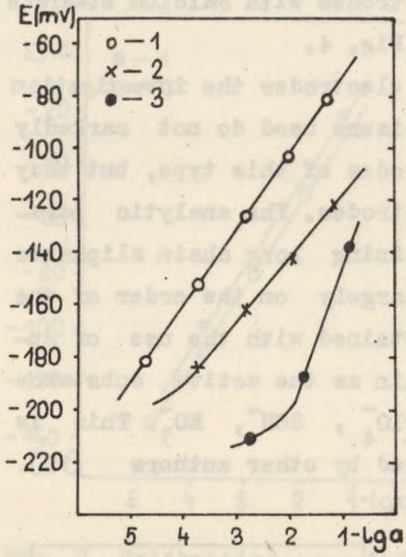

Fig. 2. Calibrating curves of BMSA-Ca-1 electrode in solutions: 1 - of primary ion, 2 - of interfering ions Mg^{+2}, 3 - of interfering ions Na^{+}

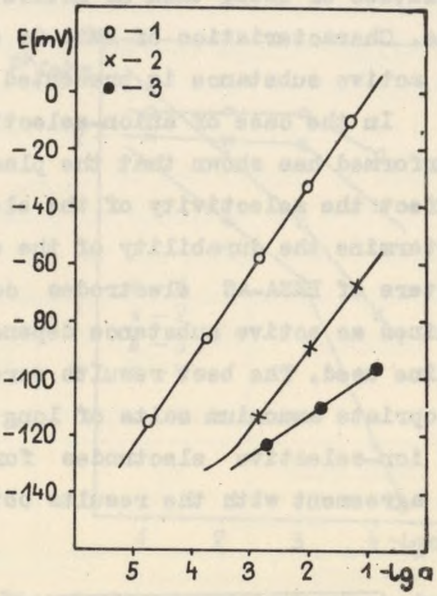

Fig. 3. Calibrating curves of BMSA-Ca-2 electrode in solutions; explanations see Fig. 2

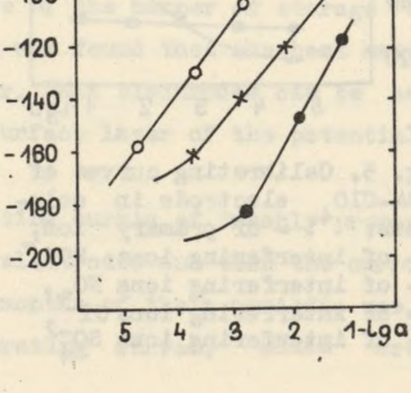

Fig. 4. Calibrating curves of BMSA-Ca-3 electrode in solutions; explanations see Fig. 2

bilities of using them as active substance in BMSA-CS electrodes. Characteristics of BMSA-Ca electrodes with calcium stearate as active substance is presented in Fig. 4.

In the case of anion-selective electrodes the investigation performed has shown that the plasticizers used do not markedly affect the selectivity of the electrodes of this type, but they determine the durability of the electrodes. The analytic parameters of BMSA-AS electrodes containing long chain aliphatic amines as active substance depends largely on the order of the amine used. The best results were obtained with the use of appropriate ammonium salts of long chain as the active substance of ion-selective electrodes for ClO_4^-, SCN^-, NO_3^-. This is in agreement with the results obtained by other authors [19].

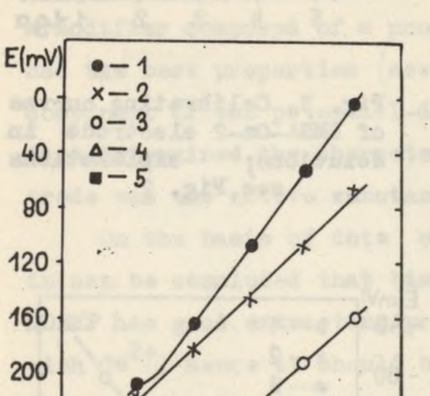

Fig. 5. Calibrating curves of BMSA-ClO_4 electrode in solutions: 1 - of primary ion, 2 - of interfering ions SCN^-, 3 - of interfering ions NO_3^-, 4 - of interfering ions Cl^- 5 - of interfering ions SO_4^{-2}

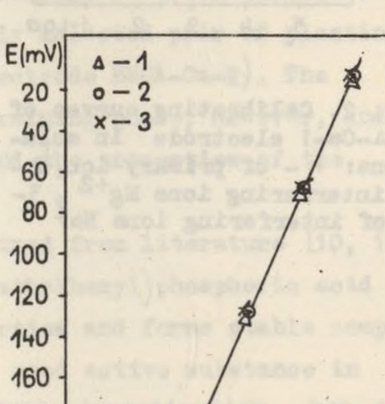

Fig. 6. Calibrating curve of BMSA-ClO_4 electrode : 1 - of freshly prepared electrode, 2 - of obtained after 1 month of use, 3 - of obtained after 2 months of use

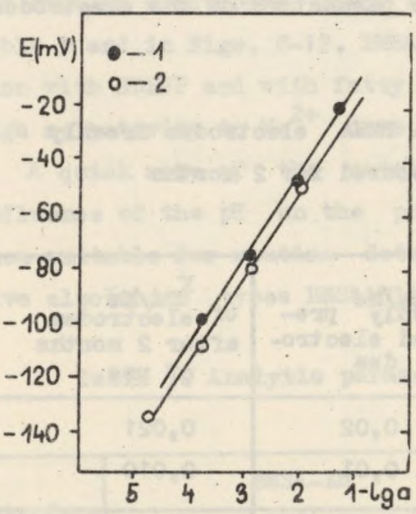

Fig. 7. Calibrating curve of BMSA-Ca-2 electrode: 1 - of freshly prepared electrode, 2 - of obtained after 2 months of use

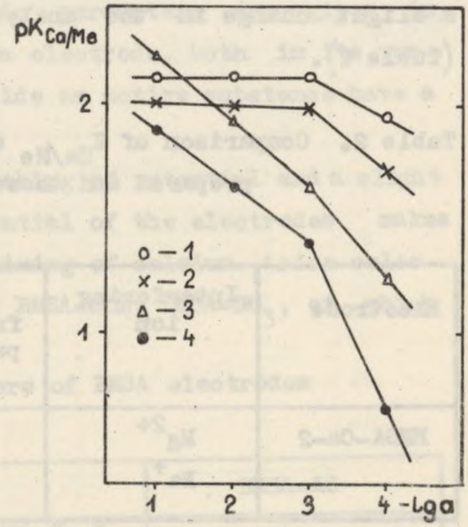

Fig. 8. Dependence of $pK_{Ca^{+2}/Me}$ on the activity of inter-fering ions electrode BMSA-Ca-1: 1 - $pK_{Ca^{+2}/Ba^{+2}}$, 2 - $pK_{Ca^{+2}/Ni^{+2}}$, 3 - $pK_{Ca^{+2}/Cu^{+2}}$, 4 - $pK_{Ca^{+2}/Mg^{+2}}$

Calibrating curves of the BMSA-ClO_4 electrode in solutions of primary ion and of interfering ions is presented in Fig. 5.

The durability of the constructed cation- and anion-selective electrodes was evaluated on the basis of electrodes and the Nerstian range of characteristics. Another problem investigated was the influence of the influence of the manner of storage on the durability of electrodes. It was found that the best manner is that of storing them in the air. BMSA electrodes can be easily regenerated by removing the surface layer of the potential-determining phase.

Figs. 6, 7 show the calibrating curves of freshly prepared BMSA-Ca electrodes and BMSA-ClO_4 electrodes and then the curves of the same electrodes after two months of their periodic use. Apart from a small shift in calibrating curves, which are characteristic of electrodes with a liquid membrane, there was a slight change in the analytic parameters of the electrodes (Table 2).

Table 2. Comparison of $K_{Ca/Me}$ of BMSA electrodes freshly prepared and those stored for 2 months

Electrode	Interfering ion	$K_{Ca/Me}$ freshly prepared electrodes	$K_{Ca/Me}$ of electrodes after 2 months of use
BMSA-Ca-2	Mg^{2+}	0,02	0,021
	Na^{+}	0,01	0,010

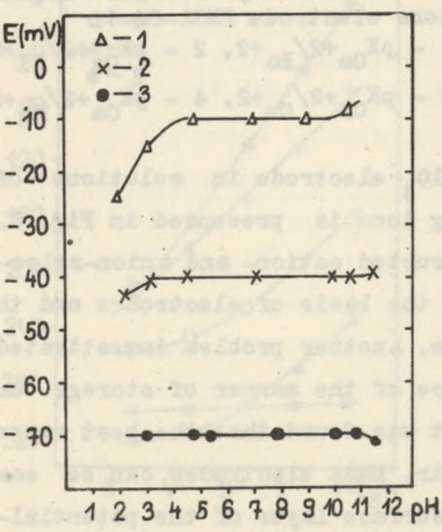

Fig. 9. Influence of pH on potential of BMSA-Ca-2 electrode; curves obtained in solution: 1 - of ions Ca^{+2} $2\cdot10^{-1}$ M, 2 - of ions Ca^{+2} $2\cdot10^{-2}$ M, 3 - of ions Ca^{+2} $2\cdot10^{-3}$ M

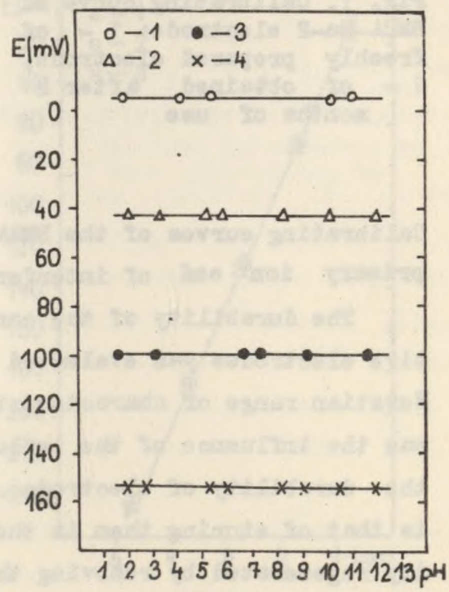

Fig. 10. Influence of pH BMSA-ClO_4 electrode; curves obtained in solution: 1 - of ions ClO_4 $2\cdot10^{-1}$ M, 2 - of ions ClO_4 $2\cdot10^{-2}$ M, 3 - of ions ClO_4 $2\cdot10^{-3}$ M, 4 - of ions ClO_4 $2\cdot10^{-4}$ M

In order to characterize more precisely BMSA-CS electrodes and BMSA-AS electrodes their basic parameters are given in Table 3 and in Figs. 8-12. BMSA-Ca electrode, both in its version with HDEHP and with fatty acids as active substance have a high selectivity to Me^{2+} ions.

A quick rate of the establishing of potential and a slight influence of the pH on the potential of the electrodes makes them suitable for routine determining of calcium. Anion-selective electrodes types BMSA-ClO_4, BMSA-SCN, BMSA-NO_3, of which

Table 3. Analytic parameters of BMSA electrodes

Interfering ion	BMSA-KS			BMSA-AS	
	BMSA-Ca-1 $K_{Ca/Me}$	BMSA-Ca-2 $K_{Ca/Me}$	BMSA-Ca-3 $K_{Ca/Me}$	Interfering ion	BMSA-ClO_4
Mg^{2+}	0,01	0,005	0,04	Cl^-	$4,2 \cdot 10^{-5}$
Ba^{2+}	0,008	0,002	0,07	NO_3^-	$2,0 \cdot 10^{-3}$
Na^+	0,05	0,005	0,13	HPO_4^{--}	$2,1 \cdot 10^{-5}$
K^+	0,01	0,0006	0,05	SO_4^{--}	$4,0 \cdot 10^{-6}$
Range of concentrations	$10^{-1}-10^{-5}$	$10^{-1}-10^{-5}$	$10^{-1}-5 \cdot 10^{-5}$		$10^{-1}-10^{-5}$
mV/px	28	29	28	*	59
Resistance 298° K/M	70	25	40		2
Time of settling of potential in solution of principal ion	60 sec.	60 sec.	90 sec.		10 sec.

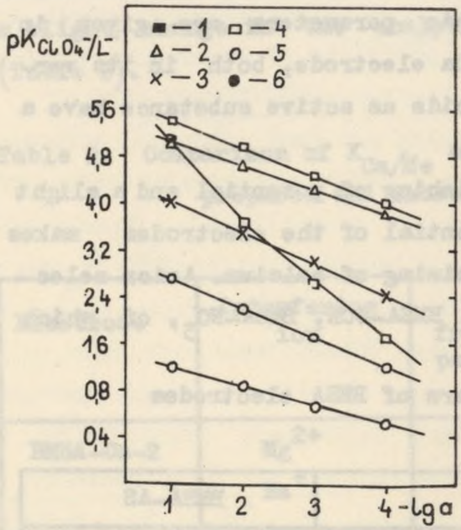

Fig. 11. Dependence of $pK_{ClO_4/L}$ on activity of interfering ions: 1 - $pK_{ClO_4'/SO_4''}$, 2 - $pK_{ClO_4'/CO_3''}$, 3 - $pK_{ClO_4'/Cl'}$, 4 - $pK_{ClO_4/H_2PO_4'}$, 5 - $pK_{ClO_4'/NO_3'}$, 6 - $pK_{ClO_4'/SCN'}$

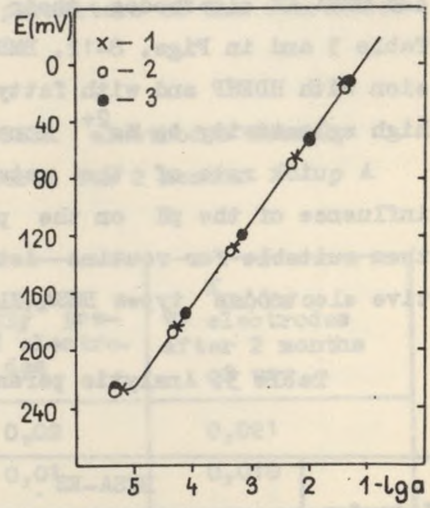

Fig. 12. Influence of ion power on potential of BMSA-ClO_4 electrode: values obtained in solutions: 1 - of ClO_4' with variable ion power, 2 - of ClO_4' I = 0.3, 3 - of ClO_4' I = 1.6

the parameters of electrode BMS-ClO_4 were given as an example, also possess very good properties (Table 4). High selectivity to ions SO_4^{-2}, CO_4^{2-}, Cl^- makes possible the determining of perchlorates in the presence of these ions. From the point of view of analytic use of special value is the wide range of pH in which the potential of the electrode was a constant value.

As can be seen from the data given here, the parameters of BMSA-CS and BMSA-AS electrodes are comparable to the data of the electrodes discussed in literature [20] and commercially available.

An analysis of the data characteristic of the BMSA electrodes shows the rightness of the assumptions concerning the construction of these electrodes: using easily accessible and cheap materials we were able to obtain ion-selective electrodes whose quality is equal to that of commercially available.

Table 4. Comparison of $K_{ClO_4/L}$ of BMSA electrode and orion 92-81 electrode

Interfering anion	BMSA-ClO_4 K_{ij}	Orion 92-81 K_{ij}
NO_3^-	2,0 x 10^{-3}	1,5 x 10^{-3}
Cl^-	4,2 x 10^{-5}	2,2 x 10^{-4}
HCO_3^-	3,6 x 10^{-5}	3,5 x 10^{-4}
SO_4^{--}	4,0 x 10^{-6}	1,6 x 10^{-4}

The investigation was subsidized from the funds of the Ministry of Science, Higher Schools and Technics and from the funds for Theme 03.10.6.05.11. The electrodes constructed have received patent protection [21, 22].

REFERENCES

1. Ross J. W.: Science 156 1378 (1967).
2. Gibson E. J. et A.L.U.S.: Patent 346759, Sept. 16, (1969).
3. Orion Research "Analytical Methods Guide". Ed. 1973, 1975.
4. Гордиевский А.В., Сырчанков А.Ю., Савинин Н.Ю., Штерман В.С., Кожухова Г.Г.: Завод.лаб. 3, 257 (1972).
5. Гордиевский А.В., Штерман В.С., Сырченков А.Ю., Савинин Н.Ю., Жукова А.Ф.: Журн. анал. хим. 3, 772 (1972).
6. Грекович А.Л., Матерова Е.А., Юринская В.Е.: Журн. анал. хим. 27, 1218 (1972).
7. Griffiths G. H., Moody G. J., Thomas J.D.R.: Analyst. London 97, 1155 420 (1972).
8. Coetze C.J., Freiser H.: Anal. Chem. 41, 1128 (1969).
9. James H., Carmack G., Freiser H.: Anal. Chem. 44, 856 (1972).
10. Cattrall R.W., Drew D.M., Hamilton I.C.: Anal. Chim. Acta 76, 269 (1975).
11. Dumkiewicz J.D.: Dissertation. Lublin 1974.
12. Dumkiewicz R.A.: Dissertation. Lublin 1975.
13. Hulanicki A.: Reakcje kwasów i zasad w chemii analitycznej. PWN, Warszawa 1972.

14. Sykut K.: Fol. Soc. Sci. Lub. 105 16 (1974): Mat. Phys. Chem. 2.
15. Frant M.S., U.S.: Patent 3406102, oct. 15 (1968).
16. Eisenmann G.: Anal. Chem. 40, 310 (1968).
17. Wise W. M., U.S.: Patent 3502560, March 24 (1970).
18. Botre M., Mascini M., Mendi A.: Anal. Chem. 44, 1371 (1972).
19. Yoshio Shijo: Bull. of the Chem. Soc. of Japon 48 5, 1647-1648 (1975).
20. Camman K.: Das Arbeiten mit jonoselektiven Elektroden. Springer - Verlag, Berlin 1973.
21. Sykut K., Dumkiewicz J., Dumkiewicz R.: Patent PRL 93560, 1975.
22. Sykut K., Dumkiewicz J., Dumkiewicz R.: Patent PRL 93227, 1975.

STRESZCZENIE

Opracowano nowy typ elektrody jonoselektywnej BMSA z pseudociekłą fazą potencjałotwórczą, którą stanowi głęboko modyfikowany plastyfikator PCW, będący zarazem nośnikiem substancji elektrodowo-aktywnej. Zbadano przydatność ciekłych kationitów oraz anionitów, rozpuszczonych w plastyfikatorach PCW, jako substancji aktywnych fazy potencjałotwórczej elektrod BMSA; badano wpływ składu jakościowego i ilościowego fazy potencjałotwórczej na własności opracowanych elektrod. W zależności od składu fazy potencjałotwórczej otrzymano elektrody kationo- i anionoselektywne o dobrych parametrach analitycznych. W pracy podano przykładowo niektóre parametry elektrod BMSA-Ca oraz BMSA-ClO_4. Opracowane elektrody cechuje prosta konstrukcja oraz dobry zespół parametrów analitycznych.

РЕЗЮМЕ

Обработано новый тип ионоселективного электрода BMSA с псевдожидкой мембраной. Исследовано возможность использования PCV в качестве активных веществ псевдожидкой мембраны электрода BMSA. Исследовано влияние качественного и количественного состава мембраны на свойства обработки электродов. В зависимости от состава мембраны получено ряд катионо и анионоселективных электродов с хорошими аналитическими параметрами. В работе представлены только некоторые параметры электродов BMSA-Ca и BMSA-ClO_4. Обработанные электроды отличаются простой конструкцией и хорошими свойствами аналитических параметров.