

IODIDE MEMBRANE ELECTRODES

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The properties of iodide electrodes depend on the ratio of γ and β -AgI in the membrane. An excess of γ -AgI causes a higher slope than the Nernstian for $pI > 5$, hence a higher sensitivity toward I^- ions. After some time and under the action of iodide solutions, the γ form is transformed into β and the elevated sensitivity disappears. In membranes composed of AgI + Ag_2S , a ternary compound, Ag_3SI , is formed which does not change with time. Their sensitivity toward light is not lower than with AgI; it is generally small in a solution of $10^{-5}M I^-$ and negligible in $10^{-5}M Ag^+$. The mechanism of the photoeffect on iodide electrodes is discussed. The observed permeability of a Crytur electrode implies a possible role of the properties of porous membranes in establishing the potential of iodide electrodes. An important factor is always the activity of ions at the solid-liquid interface. Besides the activity of ions in solution and their solubility in the membrane, also adsorption can play a significant role.

The contemporary progress in potentiometry is based on the development of new ion-selective electrodes, which was started by the preparation of heterogeneous membrane electrodes made from a silver iodide-paraffin mixture¹. These were apparently developed from silver iodide electrodes impregnated with paraffin², which was later replaced by silicon rubber³ and polyethylene⁴.

A homogeneous iodide electrode (containing only the electroactive material in the membrane) was described first by Kolthoff and Sanders⁵. A mixture of Ag_2S and AgI was proposed by Skobec and Kleibs⁶ and used later by the firm Orion⁷. Růžička and Lamm^{8,9} applied the same mixture on graphite, whereas Veselý and Jindra¹⁰ used pure polycrystalline AgI. A number of other modifications of iodide electrodes was described in the literature, *e.g.* electrodes from a silver-silver iodide mixture¹¹, those containing an iodine solution in an organic solvent¹², parchment membranes with silver iodide¹³, and the use of a Ag_2Se -AgI mixture¹⁴ or silver tetraiodomercurate¹⁵ for the determination of iodides.

Some authors studied the properties of commercial electrodes¹⁶⁻²³. Woddsen and Liebafsky¹⁶ observed a lower detection limit of an Orion electrode in nonbuffered solutions than predicted theoretically. Homogeneous electrodes have a longer life time than heterogeneous ones¹⁸, which are permeable. The properties of Crytur electrodes were discussed by Weiss¹⁹ in terms of their permeability although these electrodes are homogeneous; their permeability was considered advantageous in the

cited work because of a better reproducibility of their potential and a more rapid response.

The subject of the present work is a study of the relations between the way of preparation, porosity and electrical resistance of membranes of iodide electrodes and their response to the concentration of I^- and Ag^+ ions and to light.

EXPERIMENTAL

Potentiometric measurements were made with a digital pH meter PHM 52 against a saturated calomel electrode with a salt bridge filled with 0.1M- $NaNO_3$; potentials were recorded on an REC 51 Serverograph. The relative light sensitivity was measured on a PMT 1 Phototitrator (all from Radiometer, Copenhagen), from which the upper cover was removed and a 250 ml laboratory vessel wrapped (except for its bottom) with black paper was placed 15 mm above the top surface. The vessel was filled with a solution of $10^{-4}M-I^-$ or $10^{-4}M-Ag^+$ and the test electrode was inserted into it. The fluorescent lamp in the apparatus was then switched on and off and the potential changes of the electrode recorded. The electrode resistance was measured on a Conductoscope 81 (Laboratorní přístroje, Prague) or by the method described earlier²⁶. Iodides were determined colorimetrically by the kinetic method^{24,25} on a Spekker photometer (Hilger). Potassium was determined by the atomic absorption method on a Perkin Elmer 306 spectrophotometer connected with a pen recorder. The ionic strength of all measured solutions was kept at 0.1 by addition of $NaNO_3$. All chemicals were of reagent grade (Merck or BDH). The membrane surface was ground by an emery paper No 2/0 (SIA, Switzerland). The temperature of measurement was 25–27°C.

TABLE I
Characteristic of Electrodes Used

No	Composition	Precip. type	Pressing pressure Mp/cm ²
1	$Ag_2S + AgI$	—	12.5
2	$Ag_2S + AgI$	—	5.0
3	$Ag_2S + AgI$	—	2.5
4	AgI	<i>I</i>	8.0
5	AgI	<i>I</i>	5.0
6	AgI	<i>I</i>	2.5
7	AgI	<i>II</i>	5.0
8	$Ag_2S + AgI, 5\%PE$	—	8.0
9	$AgI/Ag_2S/AgI$	<i>II-II</i>	8.0
Crytur		—	?
53-17	AgI	—	?
Orion		—	?
94-53A	$Ag_2S + AgI$	—	?
94-53	$Ag_2S + AgI$	—	?

Measurements were performed with iodide electrodes of the type Crytur 53-17 and Orion 94-53A and 94-53. Their behaviour was compared with those prepared in the laboratory whose membranes were made by pressing the corresponding precipitates *in vacuo* (Table I). Silver iodide of the type I was prepared by mixing hot solutions of 3.83 g NaI and 4.25 g AgNO₃ in about 250 ml H₂O (iodide added into nitrate solution), *i.e.* with a small excess of iodide. The precipitate was nearly colloidal so that it could be washed five times with hot water only after two-day heating the liquid at 80°C. The precipitate was then filtered off and dried at 110°C. Silver iodide of the type II was prepared in the same way except that there was an excess of AgNO₃ (3.75 g NaI and 4.45 g AgNO₃). A mixture of AgI and Ag₂S was coprecipitated from a solution of NaI and Na₂S by addition of AgNO₃; the iodide was in a small excess. All precipitates were stored in brown bottles under exclusion of light prior to pressing. The pressure was applied gradually and its end value was maintained for five minutes. The prepared tablets were yellow and transparent or black according to composition. They were cemented to the end of poly(vinyl chloride) holders with a polysulphide glue. The membrane No 8 was made from a mixture of the Ag₂S-AgI precipitate with a solution of low-molecular mass polyethylene (Hoechst, type S 1518) in CCl₄ after evaporating the solvent to obtain a homogeneous product. The membrane No 9 consisted of three layers: both surface layers of type II AgI and a layer of Ag₂S (prepared according to ref.²⁷) between them. The internal reference electrode was of the type Ag|AgI|0.1M-KI. During studies of the permeability, also a direct silver contact was used^{10,28}.

RESULTS

Sensitivity of Electrodes toward I⁻ and Ag⁺ Ions

The thermodynamic solubility products for AgI at 25 and 35°C, pK_{s0} , are equal to about 16 (exactly 16.08 and 15.546)²⁹. Thus, the theoretical sensitivity of the electrode is characterized by $pAg = pI = 16$ with a Nernstian slope of 59.2 mV at 25°C. Assuming³⁰ that the individual activity coefficient of Ag⁺ ions in 0.1M-AgNO₃ is equal to 0.75 and that of I⁻ ions in 0.1M-NaI 0.755, then the potential difference between these solutions should be equal to 0.8150 V.

Experimental values of ΔE for the prepared iodide electrodes and Orion electrodes were in the range 0.8143-0.8228 V (*i.e.* 99.91-100.96%), hence very close to the theoretical one. The potential of two of the three Crytur electrodes in solutions of silver nitrate was, however, very variable and fluctuated around 200 mV. The potential of the third electrode (A) in these solutions was by about 20 mV more positive with respect to the other electrodes and the corresponding slope was close to the theoretical. However, the suitability of an electrode for the determination of I⁻ and Ag⁺ ions is given by its behaviour in the low concentration range, *i.e.* $pAg = 5-11$ ($pI = 11-5$). It was found experimentally that the sensitivity toward small activities of I⁻ ions is related to the "stirring effect", *i.e.* to the direction and magnitude of potential changes after the stirring is interrupted, characteristic for the given electrodes. Although the magnitude of this effect is not reproducible, its sign is preserved if the electrodes are freshly ground, and is positive or negative in solutions of 10⁻⁵M I⁻ or 10⁻⁵M Ag⁺, respectively. Within 60 s after interruption of stirring, the

potential changes were from +5 to -10 mV. An increase of potential (positive stirring effect) demonstrates itself in the same way as a drop of iodide concentration after interruption of stirring and the corresponding electrodes are characterized by a somewhat higher slope than the Nernstian at $pI = 4-6$, whereas in solutions of silver nitrate of $pAg = 4-5$ their slope is somewhat lower. The opposite case occurs with electrodes whose stirring effect is negative. Electrodes of an intermediate type can be also found showing a small positive shift in one solution and a small negative shift in another one.

The interpretation of these results is difficult. A relation exists between the way of preparation of the membrane (precipitate type) and the stirring effect, hence also the electrode sensitivity. Membranes made from AgI type *I* precipitate pressed at a higher pressure show a negative stirring effect, those from type *II* are intermediate in character. Membranes from the Ag_2S-AgI mixture pressed at a lower pressure show a negative, at a higher pressure a positive stirring effect. The sign of the stirring effect can be changed by adsorption of dissolved substances on the electrode surface and restored by grinding.

The difference between electrodes with a positive and negative stirring effect is illustrated by the dependence of potential on pAg (Fig. 1). The electrodes were ground prior to every measurement. Without this precaution, the potentials of the electrode Orion 94-53 A and of the electrodes from the precipitate *II* are shifted gradually to more negative values depending on adsorption of I^- ions on the membrane surface. Calibration curves for electrodes No 1 and 7 and for Orion electrodes after a longer contact with the iodide solution are similar to the curve for electrode No 5 (Fig. 1). In contrast, the Crytur electrode gave reproducible results. Although

TABLE II
Electric Resistance of Membranes
Values in the second column were measured after one year.

No	R , $k\Omega$		No	R , $k\Omega$	
1	5.1	4.0	7	13	40
2	5.5	4.4	8	6	4
3	5.5	4.4	9	12	71
4	35.0	117.0	Crytur (A)	130	130
5	32.0	50.0	Orion		
6	13.0	12.0	94-53A	10^a	10^a
			94-53	10	—

^a Measured with Conductoscope.

this electrode is less sensitive, it is obviously inert against adsorption from the studied solutions. The real $pAg-E$ curves obviously do not show an extremum such as in Fig. 1 at $pAg = 8$. However, it is difficult to prepare nonbuffered solutions of such a low concentration.

Ohmic Resistance of Electrodes

The resistances of the saturated calomel electrode and of the solution under study were measured separately and subtracted from the cell resistance. This was necessary since the resistance of the iodide electrodes was comparable with that of the s. c. e. The resistance of each electrode was measured twice at a year interval (Table II).

The membranes from the Ag_2S-AgI mixture show a higher conductivity than those from pure AgI as well as from pure Ag_2S^{31} . From the comparison of electrodes No 4, 5 and 6 it follows that tablets pressed at a lower pressure have a smaller resis-

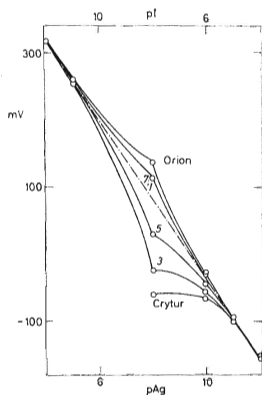


FIG. 1

Deviations from Nernstian Dependence at $pAg = 5-11$ for Selected Electrodes

A solution of $0.1M-NaNO_3$ was used in the case $pAg = 8$.

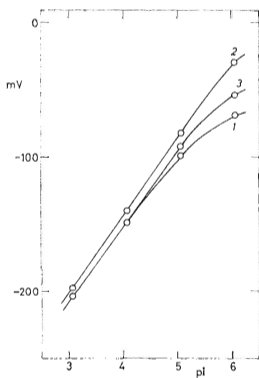


FIG. 2

Permeability of Crytur Electrode

1 Original $pAg-E$ curve of commercial electrode (with internal reference solution); 2 after remounting the membrane into another holder (with internal silver contact); 3 after remounting the membrane into another holder (with internal reference solution) and aging for 72 h.

tance. Addition of polyethylene into the tablet material does not cause an increase of the electric resistance (electrode No 8 is a heterogeneous one). Both types of Orion electrodes showed an equal resistance; the resistance of the newer type (94-53 A) must be measured with an a.c. bridge since the passage of a direct current of the order of several μA causes irreproducible electrode potential values during several hours or even a day. This does not occur with the older Orion 94-53 electrode. The resistance of AgI membranes pressed at a higher pressure than about $2.5 \cdot 10^3 \text{ kp/cm}^2$ increased after one year in proportion to the pressure used. At the same time, the membranes changed their appearance and became dull (*e.g.* No 4 and 5). A similar process took place in membranes No 7 and 9, which had another composition.

Sensitivity of Electrodes to Light

A change in illumination by about 400 lux causes a change in the electrode potential, which attains a stationary value after 5-10 min. In the iodide solution (Table III), the largest photosensitivity was observed with the Orion 94-53 A electrode. The Crytur (A) electrode was approximately as sensitive as the older Orion 94-53. Electrodes most sensitive to light were also most sensitive to I^- ions at about $\text{pI} = 5$. An exception was electrode No 9, which was relatively little sensitive to light and highly sensitive to I^- ions, whereas it responded more slowly to changes in ionic activity. The photosensitivity in a stirred solution differs only little from that in a quiet one. With increasing light intensity, the potential is always shifted to more positive values, and in an analogous experiment in a silver nitrate solution the photosensitivity for all electrodes was lower than 1 mV. The photoeffect is therefore basically related to the value of pAg in the solution.

TABLE III

Sensitivity of Electrodes to Illumination (about 400 lux)

I The solution of 10^{-4}M-NaI was not stirred during measurement; II the solution was stirred.

No	ΔE , mV		No	ΔE , mV	
	I	II		I	II
1	+11.5	—	7	+13.5	—
2	13.3	12.0	8	0.9	—
3	1.8	3.1	9	5.4	—
4	3.0	3.0	Crytur	9.1	8.3
5	7.7	7.4	Orion		
			94-53A	15.4	13.9
6	4.5	2.4	94-53	8.3	9.1

Permeability of Membranes of Iodide Electrodes

One electrode Crytur (A) and all prepared electrodes were dipped into 20 ml distilled water for 48 h and the content of I^- and K^+ ions in the aqueous phase was determined. Each electrode was eluted twice. In the first test, the electrode tubes were filled with 0.1M KI as internal electrolyte and in the second a silver contact was used instead.

The different low contents of I^- ions in the eluate (Table IV) can be attributed to desorption, contamination and experimental errors. The amount of 0.25 $\mu g I^-$ in 20 ml corresponds to $10^{-7} M I^-$, so that the lowest concentrations are influenced by the solubility of AgI. Significant contents of I^- ions were found in the eluates from electrodes No 2, 3, 5 and Crytur with internal electrolyte. In the case of electrodes with silver contact, the contents of I^- ions in the all eluates were low. The eluates from electrodes No 2, 3, 7 and Crytur contained 8.05, 7.98, 8.21 and 5.63 $\mu g K^+$ in 20 ml. For other electrodes with an internal electrolyte and for those with a silver contact, values lower than $10^{-6} M K^+$ (0.78 $\mu g K^+/20 ml$) were found. The determination of potassium by atomic absorption is less sensitive than the used determination of I^- ions, nevertheless the results are again an evidence for the permeability of electrodes No 2, 3 and Crytur. However, the amount of K^+ ions found in the eluate from electrode No 5 was comparable with that of I^- ions. The opposite case occurred with electrode No 7. With the Crytur electrode, the contents of K^+ and I^- ions correspond approximately to each other and the electrode is permeable for potassium iodide. Its amount passed into the solution during an hour corresponds to about $3 \cdot 10^{-3} \mu l$ of 0.1M-KI (*i.e.* of the internal electrolyte), hence the diffusion is very slow. The diffusion of K^+ and I^- ions through the membranes No 5 and 7 did not proceed evenly.

The permeability of the Crytur 53-17 electrode was proved experimentally also

TABLE IV

Determination of Iodides

A With internal reference solution; B with internal silver contact. Electrodes were leached in distilled water for 2 days prior to measurement.

No	$\mu g I^-/20 ml$		No	$\mu g I^-/20 ml$	
	A	B		A	B
1	0.23	0.13	6	0.25	0.66
3	7.8	0.20	7	0.26	0.30
3	4.8	0.60	8	0.10	0.24
4	0.27	0.28	9	0.12	0.14
5	5.8	0.14	Crytur (A)	21.3	0.39

after the membrane was cemented into another holder enabling to use both systems, an electrolytic as well as a silver contact, and their simple exchange. In the case of a silver contact, the sensitivity was higher by about one pI unit as compared with the original construction (with the internal reference electrolyte). If the internal AgI electrode was used again, the higher sensitivity of the electrode was maintained for more than 24 h. However, during repeated measurement after another 48 h the electrode showed a decreased sensitivity and a negative stirring effect even when the calibration curve did not attain the original form (Fig. 2).

DISCUSSION

The preparation of iodide electrodes from silver iodide is complicated mainly by its polymorphism. Two modifications exist at ambient temperature differing by their structure, properties and volume^{32,33}. The hexagonal β modification with a wurtzite structure is formed by precipitation in the presence of an excess of I^- ions, whereas the cubic γ -AgI of a sphalerite type lattice is formed in the presence of an excess of nitrate ions. In the isoelectric point (*i.e.* at $6.2 > pAg > 6.0$) the AgI precipitate is a mixture of approximately equal amounts of both modifications³⁴⁻³⁶. The third one, α -AgI, is stable only above $146 \pm 1^\circ C$, has a cubic lattice and a very high ionic conductivity.

Thus, the precipitate *I* used for electrode membranes No 4-6 contains a high amount of β -AgI and the precipitate *II* (electrodes No 7 and 9) mostly γ -AgI. The ratio of both modifications in the electrode membrane, however, is given not only by the method of preparation of silver iodide but depends also on the pressing pressure and time. At a pressure higher than about 2500 kp/cm² and at 30°C, β -AgI changes³³ to γ -AgI. Since the latter is unstable at normal conditions³⁷, it changes slowly to β -AgI expanding in volume. Volume changes occur also during conversions³³ of α -AgI to β and α -AgI to γ , and cause undesirable destruction of AgI crystals grown by the Stockbarger method³⁸ during cooling. It is therefore not possible to use AgI crystals in the preparation of iodide electrodes similarly as with silver chloride and bromide¹⁰.

Based on the mentioned facts, most of the presented experimental results can be explained. To prepare iodide electrodes from silver iodide, γ -AgI is recommended from the point of view of sensitivity. Membranes containing this modification show positive deviations from the Nernstian potential dependence in the range $11 > pAg > 5$. At $pI > 5$, the slope of the iodide electrode characteristic is higher than according to the Nernst equation (59.2 mV/pI). This supersensitivity effect⁹ has not been according to the author's knowledge described in the literature in the case of membranes containing a single chemical compound. During a longer contact with an iodide solution, γ -AgI changes to β -AgI as evidenced earlier by electrography³⁹, and simultaneously the supersensitivity effect gradually disappears, especially when the

membrane is not regularly renewed (*e.g.* by grinding with an emery paper). Since the conversion of the metastable γ -AgI to β -AgI proceeds probably slowly also inside the tablet and can be accelerated in the case of permeable electrodes by contact with the internal reference iodide solution, mechanical grinding of the surface has only a temporary effect. After some time, the behaviour of membranes containing originally γ -AgI becomes more and more similar to those from β -AgI, which at $pI > 5$ show negative deviations from the theoretical potential. Hence, the supersensitivity effect of silver iodide electrodes is a transient phenomenon. Besides that, the volume expansion during the conversion of γ to β -AgI may lead to the formation of very fine pores inside the membrane causing permeability and a decrease in contact surface conductivity in the membrane. According to Hull and Pilla⁴⁰, the internal conductivity of AgI is $10^{-8} \text{ ohm}^{-1}\text{cm}^{-1}$ at ambient temperature, and higher values in the polycrystalline material are caused by the contact conductivity. Changes in the resistances of electrodes No 4, 5, 7 and 9 can be attributed to a decrease in their contact conductivity.

Membranes prepared from precipitate I may contain prevalingly β -AgI or, if the pressure of 2500 kp/cm^2 was exceeded, also γ -AgI. In agreement with literature data, the membrane of electrode No 6 does not practically change with time since it contains β -AgI, which is stable at normal temperature. The stability of membranes from β -AgI, which is advantageous, is however accompanied by their lower sensitivity against iodides. In addition, the pressure range for the manufacture of tablets from β -AgI is very narrow; pressures lower than about 2000 kp/cm^2 do not lead to the formation of compact, mechanically resistant and transparent tablets, whereas pressures higher than 2500 kp/cm^2 cause the formation of γ -AgI.

Interpretation of the properties of Crytur 53-17 iodide electrodes has been already extensively discussed. The permeability of their membranes with respect to potassium iodide solutions appears now as an experimental fact in accord with the assumption of Weiss¹⁹. The Crytur electrode membranes are apparently composed mainly of β -AgI (since no changes in their electrical resistance were observed) and were pressed in air atmosphere at a pressure lower than 2500 kp/cm^2 . The lower pressure, air bubbles and the corresponding bad coherence are probably the reason for diffusion of the internal electrolyte through the membrane.

Iodide electrodes from the $\text{Ag}_2\text{S-AgI}$ mixture do not change their properties with time, which is their great advantage. Their high electrical conductivity (of the order of $10^{-4} \text{ ohm}^{-1}\text{cm}^{-1}$) suggests that the tablets contain the ternary compound⁴¹⁻⁴³ Ag_3SI . Our experiments show that for good electrodes of this type pressing pressures higher than 5000 (or possibly 8000) kp/cm^2 are necessary. It is probable that the Orion electrodes are prepared similarly as electrode No 1 since their membranes have similar properties. The 94-53 A electrode, however, in contrast to the older type 94-53, does not contain an internal electrolyte as follows from its behaviour during passage of d.c. current. The internal metallic contact in the newer electrode

type is preferable since it eliminates any contamination of the measured solution by the internal reference solution. Reasons for the nonreproducible behaviour of 94-53 A type electrodes during passage of d.c. current are related to polarization of the ionic-metallic conductor interface, a relatively little investigated phenomenon.

The sensitivity of iodide electrodes to light has been often discussed in the case of the classical AgI electrodes⁴⁴. Our experiments confirm the dependence of the potential of all studied iodide electrodes on the light intensity, but this effect is not large and is very different for different electrodes. A lower photosensitivity of Ag₃SI membranes against AgI assumed by some authors^{7,45} was not observed.

The mechanism of the photosensitivity can be discussed in terms of solid state physics. A possible explanation is based on changes in concentration of interstitial Ag⁺ cations. These and the silver vacancies are cations and anions in the solid state, similarly as H⁺ and OH⁻ ions in solutions. Interaction of light with the membrane produces photoelectrons close to its surface. In an iodide solution, where the iodide electrode functions as anode of a galvanic cell, these mobile electrons diffuse into the membrane, where they recombine with interstitial Ag⁺ ions to give Ag atoms. The decrease in concentration of interstitial Ag⁺ ions in the solid phase causes (according to Hoffman⁴⁶) a shift of the electrode potential to more positive values. If the electrode functions as cathode of a galvanic cell, which is the case in silver nitrate solutions, the photoelectrons are held by electrostatic forces near the membrane surface, hence no appreciable decrease in the concentration of Ag⁺ ions in the solid phase occurs. (The photosensitivity of Ag₃SI was discussed analogously by Kennedy and Boodman⁴⁷.)

The potential-determining process on iodide electrodes is obviously rather complicated. In the most general case, the potential can be influenced by the properties of the porous membranes as well as by phenomena occurring in the solid-liquid interface²⁰. Our experiments show that the use of thermodynamic constants is not sufficient to describe the properties of such electrodes. An important potential-determining factor is only the activity of ions in close proximity of the solid surface, which is in the ideal case given by the activity of ions in the solution and solubility product of the chemical compound in the membrane. In most cases, however, it is higher or lower according to whether the membrane has an excess of silver or iodine on its surface or inside and whether the surface activity increases or decreases by diffusion of the internal reference electrolyte through the membrane. The situation at the electrode surface can be judged from the "stirring effect" while the behaviour of the membrane in diluted solutions after grinding yields information about electrochemical properties of the precipitate in the membrane. The positive and negative deviations in Fig. 1 cannot be therefore interpreted as nonfulfilment of the Nernst equation since they are only apparent. In addition to the curvature of the calibration curve and loss of sensitivity of the electrode attributed to the influence of solubility of the membrane (subsensitivity effect), also the opposite, supersensitivity effect

must be considered. The latter is accompanied by lowering of the measured ionic activity at the electrode surface against the bulk of the solution, and this either as a result of the presence of another, more soluble compound in the membrane⁹ or as a result of adsorption or desorption from the membrane. In the case of silver iodide, the deviations from the theoretical potential can be attributed to the formation of β - and γ -AgI on the membrane surface, their different composition, adsorption properties, and perhaps solubility. Also the standard potentials of β - and γ -AgI may be different⁴⁶. The fact that similar deviations were found already earlier with silver iodide electrodes^{2,48} confirms again their relation to membrane electrodes. The classical "wire" electrodes, which have been used in potentiometry for several tens of years⁴⁹, differ from membrane electrodes only by their higher sensitivity toward oxidizing or reducing compounds⁵ and sometimes by the reproducibility of their potentials.

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