Chapter 3
Ion-Selective Electrode Characteristics

This chapter is devoted to practically relevant characteristics of ISEs and to the methods of the experimental assay of these characteristics. For the practical use of ISEs, we have to know the working range and the response slope of the sensor, its' selectivity, response time, and the stability of these characteristics over time and their reproducibility from one replica electrode to another one.

The methods of the experimental assay of these characteristics are the same whatever is the ISE, whether it is with a polymeric, or a glass, or a crystalline membrane. Therefore, these methods are discussed in this chapter, which precedes chapters devoted to certain types of ISEs.

3.1 Ion-Selective Electrode Working Range and Response Slope

Basically, the ISE working range and response slope are determined directly from the calibration curve. The working range is characterized by the lower and the upper detection limits of the ISE. Traditionally, these limits were defined by IUPAC [1] and Buck and Lindner [2] as the values of the concentrations (activities) of the target analyte where the error of the analysis equals 100 %. This definition implies that the measured concentration (activity) is twice larger or twice lower than the target value. Bearing in mind the Nernst equation and the IUPAC definition of the detection limit, one can see that ΔE deviation of the measured EMF from the straight line in the detection limit is:

$$\Delta E = \pm \frac{\mathrm{RT}}{z_I F} \ln \frac{a^{\mathrm{measured}}}{a^{\mathrm{target}}} = \pm \frac{\mathrm{RT}}{z_I F} \ln 2 \tag{3.1}$$

The "+" sign refers to the lower and the "−" sign to the upper detection limit. Thus, at room temperature, for an electrode selective to a univalent ion, the lower detection limit refers to the deviation of approx. +18 mV, and in the case of a divalent ion—to approx. +9 mV. These deviations are significantly higher than the typical value of the experimental error. Therefore, the advantage of in this way

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defined detection limits is low sensitivity to the inevitable random errors of the EMF measurements, see Fig. 3.1.

The linear range can be considered as the linear part of the calibration curve, that is, the part where the deviations from the linearity do not exceed the measurement error. Therefore, in contrast to the working range, the linear range is very sensitive to the value of the measurement error, and it is always narrower than the working range.

The working (and also the linear range) of an ISE may depend on the particular electrolyte, that is, on the nature of the anion for a cation-selective electrode and the nature of the cation for an anion-selective electrode. This is especially important for ISEs with ionophore-based membranes. In electrolyte solutions with lipophilic anions, the upper detection limit of cationic electrodes shifts to lower concentrations when compared with electrolytes containing only hydrophilic anions, for details see Sect. 4.4.4.

Recently, the traditional IUPAC definition of the detection limit was put under question. This happened for two reasons. One reason is connected to the progress in the improvement of the lower detection limit [3, 4]. Various approaches allow for the drastic expansion of the working range, see Sect. 7.2. However, the ISE response within this expanded range, typically, is not linear, and the calibration curve contains a super-Nernstian part (see Fig. 3.2). The traditional definition of the detection limit is not consistent with the super-Nernstian response curve. Indeed, the ISE presented in Fig. 3.2 is responding down to 10^{-10} M, and the readings deviate from the ideal Nernstian line to the negative direction which is in contrast to the calibration curve with an ordinary detection limit.

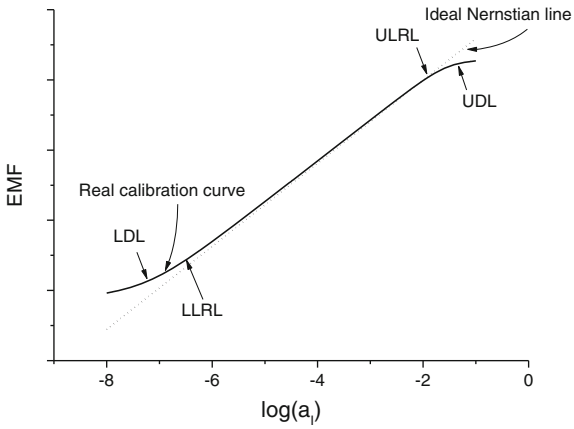

Fig. 3.1 Example of the ISE response span and slope. The ideal *Nernstian straight line* is plotted with the slope $S = \mathrm{d}E/\mathrm{d}\log a_I = 59.2$ mV. The *real calibration curve* has the slope $S = 57.2$ mV within the linear range from $\log a_I = -6.2$ (lower linear range limit—*LLRL*) to $\log a_I = -2.0$ (upper linear range limit—*ULRL*). The lower detection limit (*LDL*) is $\log a_I = -6.8$, and the upper detection limit (*UDL*) is $\log a_I = -1.2$

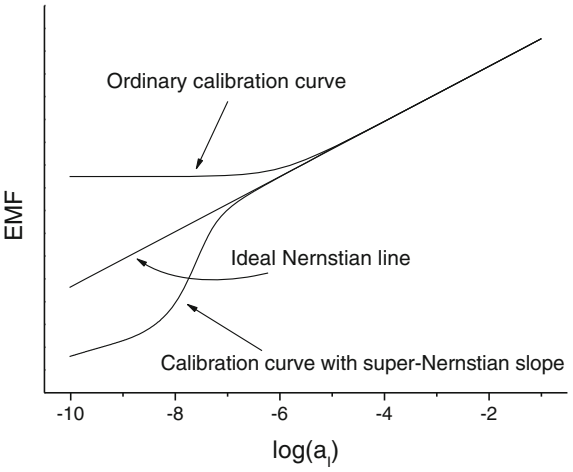

Fig. 3.2 Schematic plot of the ideal Nernstian response, a calibration curve with the ordinary lower detection limit, and a calibration curve with a super-Nernstian part

The other reason is that the IUPAC definition of the detection limit is not consistent with the respective definitions used in other branches of science, where the detection limit is affixed to a certain ratio of the reading value over the standard measurement error. Nevertheless, the traditional definition remains widely recognized and used.

3.2 Potentiometric Selectivity Coefficient

The potentiometric selectivity of an electrode is its ability to respond only to the target analyte ion in the presence of other ions. In other words, if the activity of the target ion is the same, the electrode potential and the measured EMF (ideally) are also the same whatever is the composition of the sample. Importantly, the potential of an ideally selective electrode is constant at a constant activity of the analyte, but not necessarily at a constant concentration. If the concentration of the target analyte ion is the same, but concentrations of other ions vary from sample to sample, the activity coefficients of all the ions also vary. Therefore, the activity of the analyte ion, and the respective electrode potential, also varies even in the hypothetical case of the ideal selectivity. The practical approaches to overcome this problem are discussed in Sect. 9.1.

The selectivity of the real-world electrodes is far from being ideal. The glass pH electrode and, to lesser extent, the fluoride-selective electrode with membrane made of mono-crystalline LaF_3 doped with EuF_2 can be considered as exceptions. The selectivity of these electrodes to the pH and to F^- ions is extremely high. The selectivity of other electrodes is limited. Normally, the selectivity of an electrode is quantified on the basis of the Nikolsky equation. This equation already appeared in Eq. (1.5) and is presented here for the readers' convenience:

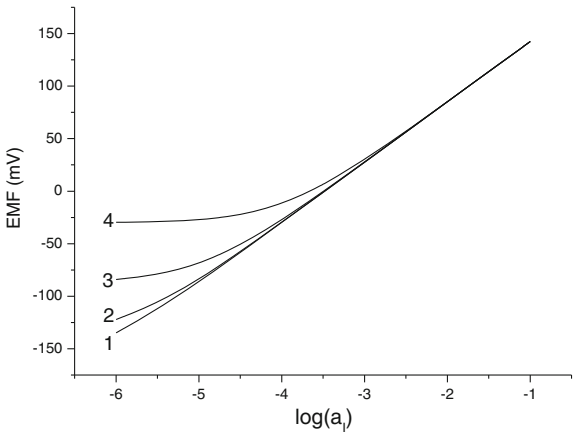

Fig. 3.3 The ISE response in mixed solutions IX + JX electrolytes with constant activity of J^+ interfering ions: $a_J = 0.1$. The ISE obeys the Nikolsky Eq. (3.2) with the following parameters: $E^0 = 200$ mV, $S = 57.5$ mV/ log a_I. *Curve 1* refers to pure IX solutions, *curves 2–3* to solutions with $a_J = 0.1$ M. Selectivity coefficients are 10^{-5} (*curve 2*), 10^{-4} (*curve 3*), 10^{-3} (*curve 4*)

$$E = E^0 + S \log \left(a_I + K_{\mathrm{IJ}} a_J\right) \tag{3.2}$$

The quantitative measure of the selectivity is the selectivity coefficient: the parameter K_{IJ} in the Eq. (3.2). In fact, this equation can only be applied if both I^{z_I}, the primary (target analyte) ion, and J^{z_J}, the interfering ion have equal charges. The role of the selectivity coefficient is illustrated by Fig. 3.3. One can see how the selectivity affects the ISE response range in mixed solutions. Even in the case of relatively high selectivity, $K_{\mathrm{IJ}} = 10^{-3}$, the linear range of the ISE in mixed solution with 0.1 M interfering ions is drastically narrower than in pure IX solutions.

Quantification of the selectivity to differently charged ions relies on different equations. Historically, the selectivity to I^{2+} divalent cations (or anions) in the presence of J^+ monovalent cations (anions) has been described by equation recommended in 1975 by IUPAC [1]:

$$E = E^0 \pm \frac{\mathrm{RT}}{2F} \ln\left(a_I + {K_{\mathrm{IJ}}}^{\mathrm{IUPAC}} {a_J}^2\right) \tag{3.3}$$

Another equation to describe the same case was proposed by Buck and Stover [5]:

$$E = E^0 \pm \frac{\mathrm{RT}}{F} \ln\left(a_I^{1/2} + {K_{\mathrm{IJ}}}^{\mathrm{Buck}} a_J\right) \tag{3.4}$$

Sign + refers to cation-responding ISEs, and sign − to anion responding. These equations neither have clear theoretical background, nor fit experimental data, although are often called "semi-empirical." Both Eqs. (3.3) and (3.4) look similar to the Nikolsky equation and transform into the Nernst equation if either a_I or a_J is zero, that is, in pure solutions of IX_2 or JX electrolytes. Unlike the Nikolsky

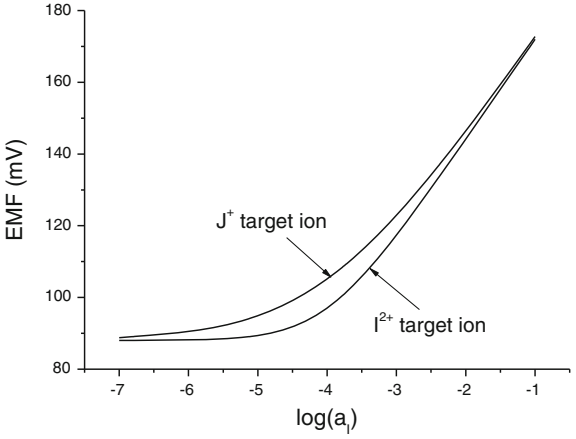

Fig. 3.4 Calibration curves calculated by IUPAC Eq. 3.3) for mixed solutions of IX_2 and 0.1 M JX electrolytes, considering as the target analyte either I^{2+} or J^{+} ions

equation, Eqs. (3.3) and (3.4) are sensitive to whether I^{2+} divalent ion is the target and J^{+} monovalent ion is the interference, or vice versa [6], see Fig. 3.4.

One can see that the respective curves calculated for mixed solutions do not coincide, except of the domains of full I^{2+} or full J^{+} response.

First Morf [7] and later (in a different way) Bakker et al. [6] derived another equation to describe the potentiometric selectivity toward divalent primary ions in the presence of monovalent interference:

$$E = E^0 + \frac{\mathrm{RT}}{F}\ln\left(\sqrt{a_I + \frac{1}{4}{K_{\mathrm{IJ}}}^{M-B}{a_J}^2} + \sqrt{\frac{1}{4}{K_{\mathrm{IJ}}}^{M-B}{a_J}^2}\right) \tag{3.5}$$

The selectivity coefficient here $({K_{\mathrm{IJ}}}^{M-B})$ is denoted here with upper index $M-B$, after Morf and Bakker, in order to distinguish between selectivity coefficients which appear in Eqs. (3.3) and (3.4).

The equation for the response to a monovalent primary ion in the presence of a divalent interference also was derived by Bakker et al. [6]:

$$E = E^0 + \frac{\mathrm{RT}}{F}\ln\left(\frac{a_I}{2} + \frac{1}{2}\left({a_I}^2 + 4{K_{\mathrm{IJ}}}^{B}a_J\right)^{1/2}\right) \tag{3.6}$$

Equations (3.5) and (3.6) are symmetric and are not sensitive to which ion is considered target and which one is interference. Unfortunately, the theoretical derivation of Eqs. (3.5) and (3.6) relied on the complete dissociation of the electrolytes in the membrane phase. This assumption is hardly true for real ISE membranes, especially for divalent ions. However, these equations are suitable for the practical use.

3.3 Measurements of the Selectivity Coefficients

Describing the principles of the experimental estimation of the selectivity coefficients, we will rely on the Nikolsky equation. The measurements of the selectivity coefficients for ions of non-equal charges are performed in analogous ways. For more detailed discussion on various methods of the selectivity coefficients measurements, see [8, 9].

3.3.1 Separate Solutions Method

Currently, the *separate solutions method* (sometimes called the *bi-ionic potentials method*) is predominating among other experimental techniques aimed at the assay of the selectivity coefficients. The basic idea of the method is very simple. If we measure the ISE potentials in a series of pure IX electrolyte solutions (I^+ is the target ion), and the electrode obeys the Nikolsky equation, the EMF follows the equation below:

$$E_I = E^0 + S \log a_I \tag{3.7}$$

The EMF measured for pure JX, the electrolyte containing J^+ interfering ions, according to the Nikolsky equation is as follows:

$$E_J = E^0 + S \log \left(K_{\mathrm{IJ}} a_J\right) \tag{3.8}$$

For the EMF values registered separately in pure IX and JX solutions with equal values of the primary and interfering ion activities ($a_I = a_J$), we have:

$$\log K_{\mathrm{IJ}} = \frac{(E_J - E_I)}{S} \tag{3.9}$$

Thus, calibrating the ISE in two pure electrolyte solutions: IX and JX, one can obtain both the calibration parameters of the electrode (E^0, S) and also the selectivity coefficient. The method is illustrated by Fig. 3.5.

The problem is that the real-world ISEs do not obey the Nikolsky equation quantitatively. That is, the respective calibration curves are not parallel, see Fig. 3.5, and the values of the selectivity coefficients depend on the particular values of $a_I = a_J$ chosen for the calculations. Normally, the calibration curve obtained in pure IX (target ion) electrolyte is linear, and the slope is close to the theoretical Nernstian value: $S \approx 2.303\,\mathrm{RT}/z_I F$. Special protocols of the ISE conditioning and of measurements allow for nearly Nernstian slope also in the JX (interfering ion) electrolyte, see Sect. 3.3.4. Otherwise, the calibration curve measured in JX electrolyte is nonlinear, and if it contains a linear part, the slope is rather sub-Nernstian. The curves converge in the diluted solutions, like shown in Fig. 3.5. Therefore, the values of the selectivity coefficients measured using the

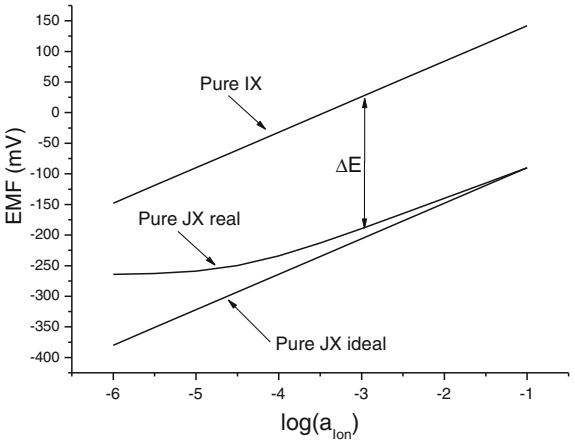

Fig. 3.5 Separate solutions method. The data refer to $K_{IJ} = 10^{-4}$

respective deltas of the EMFs are strongly dependent on the concentrations of the electrolytes. More of this, it becomes unclear which value of S must be set into Eq. (3.9): the slope obtained in pure IX or that obtained in pure JX. Normally, the slope measured in IX is set in calculations. The values of the selectivity coefficients measured at higher concentrations are more "optimistic," while measurements at lower concentrations show worse selectivity of the ISE. Typically, the selectivity coefficients are roughly independent on the ions concentrations in the cases of moderate selectivity, when $\log K_{IJ} > -2$. The origin of the variability of the K_{IJ} values and the way of how to obtain the so-called unbiased selectivity coefficients is discussed below.

The practical solution of the problem of the non-constancy of the K_{IJ} values is quite obvious. If a study is undertaken for a certain kind of samples (e.g., technological fluids in a certain industrial process, or soils originating from the same region, or waste waters from the same factory), the compositions of the samples vary in a relatively narrow range. One therefore has to measure the selectivity under the particular conditions typical for this kind of samples. In this way, obtained selectivity coefficients can be used to see whether the ISE will provide with reliable data. In some cases, when the activity of the interfering ion is known, it is possible to introduce the correction for the interference using the value of the selectivity coefficient.

3.3.2 Fixed Interference Method

The separate solutions method relies on measurements in pure solutions. Therefore, it is often criticized as being non-adequate since the selectivity is the ability of an ISE to distinguish between ions in mixtures. Measurements in mixed solutions are performed with either (1) variable concentration of the target analyte ions

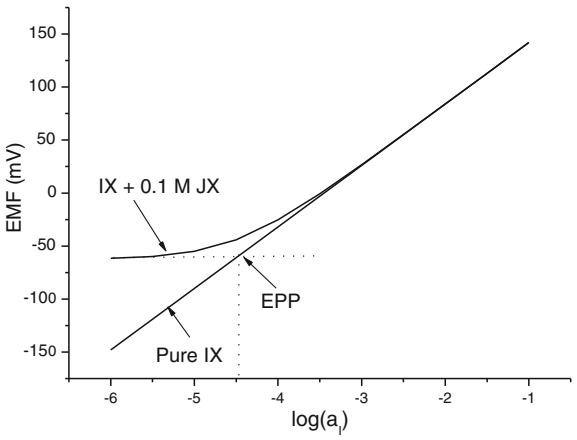

Fig. 3.6 Fixed interference method. The data refer to $a_I = 0.1$ M, $K_{IJ} = 3 \cdot 10^{-4}$

and a constant concentration of the interference, the so-called *fixed interference method* (FIM), or (2) in another way round: with variable concentration of the interference at a constant level of the primary ion. The first option is represented in Fig. 3.6.

As shown in the figure, the linear range of the ISE response in pure solutions of IX (primary ion electrolyte) is wider than that in mixed solutions containing also JX interfering ion electrolyte. With dilution in IX, the curve measured in mixed solutions deviates more and more from the Nernstian line and finally gets flat at low concentrations of IX. The calibration plot contains two straight lines: the Nernstian (or near-Nernstian) response to the target ion and the horizontal line when the ISE potential is determined by the interfering ion. The intercept point of these two lines refers to equal values of the EMF obtained for pure IX solution and for mixed solution with $a_I \ll K_{IJ} a_J$. Thus, for the EMF in this point (the equipotential point—EPP), the Nikolsky equation gives:

$$E = E^0 + S \log a_I{}^{\text{epp}} \tag{3.10}$$

and also

$$E = E^0 + S \log (K_{IJ} a_J) \tag{3.11}$$

The selectivity coefficient equals the ratio of the respective ion activities:

$$K_{IJ} = \frac{a_I{}^{\text{epp}}}{a_J} \tag{3.12}$$

One can also solve the Nikolsky equation for the selectivity coefficient in all the points where the deviations from the linear response significantly exceed the experimental error. Then, the selectivity coefficient can be calculated according to the following equation:

$$K_{\mathrm{IJ}} = \frac{10^{\frac{E-E^0}{S}} - a_I}{a_J} \tag{3.13}$$

Here, E stands for the EMF value measured for the particular values of a_I, a_J in mixed solution.

Although the mixed solutions method is often considered as more reliable than the separate solutions method, obtaining constant values of the selectivity coefficients requires special measures described in Sect. 3.3.4. Otherwise, the FIM method suffers the same problem as the SSM method: the selectivity coefficients depend on the measurements conditions. Calculations using Eq. (3.13) show more "optimistic" values of the selectivity coefficients for lower concentrations of the primary ion in mixed solution. It may seem this trend is in contrast to that typical for the separate solutions method. In fact, the numerical values of K_{IJ} obtained by FIM using a certain a_J value approach those obtained by SSM with the same activity of the interfering ion. If measurements are made in several series of mixed solutions which differ in the value of the fixed concentration of the interference, the results are completely consistent with those obtained by the separate solutions method. Like in the case of SSM, the results obtained for higher values of the interfering ion concentration yield better selectivity coefficients. The fixed interference method consumes more time and labor and therefore is less in use than the separate solutions method.

Practical recommendations to circumvent the problem of the variability of the selectivity coefficients are the same as in the case of the separate solutions method. The particular value of the fixed concentration of the interference in mixtures should not be chosen arbitrarily, but should be typical for the particular kind of samples to be analyzed.

The other option of the mixed solution method: when the primary ion concentration is fixed, and the interfering ion concentration is varied, nowadays is used almost exclusively to characterize the working pH range of an ISE. In this case, the selectivity coefficient is only rarely calculated, rather the range of the pH when the ISE potential remains unaltered is reported. For instance, the data presented in Fig. 3.7 suggest the working pH range of the ISE is 2–9.

The lower pH limit strongly depends on the nature and the composition of the ISE membrane. In many cases, it is determined by the interference from hydrogen ions with the ISE response. However, the upper pH limit for most of ISEs (except of the pH electrodes) is roughly the same: pH 9–10. In the case of crystalline electrodes selective to heavy metal cations, this is, at least partly, due to the solution chemistry: ions produce hydroxides and therefore concentrations of free ions decrease. In the case of ISEs with solvent-polymeric membranes selective to alkaline and alkaline-earth cations, and to various anions, the upper pH limit may be due to saponification of the membrane plasticizers and therefore is virtually independent on the nature of the ionophore.

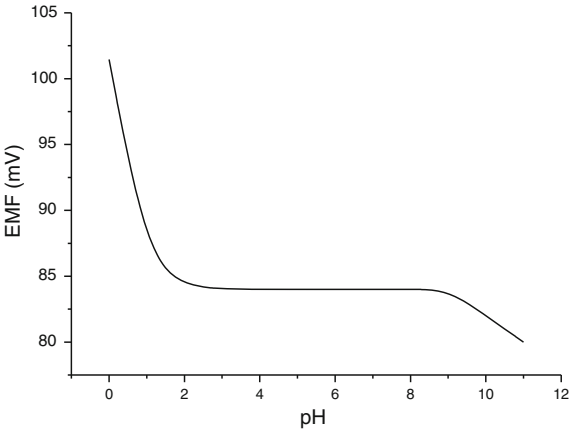

Fig. 3.7 The working pH range

3.3.3 Matched Potentials Method

The matched potential method (MPM) does not rely on any theory and does not assume a certain equation describing the ISE response in a mixed solution. The method is based on a procedure of measurements of the potential differences caused by increase in the target analyte activity in solution and that due to increase in the interfering ion activity. The MPM measurements procedure is as follows: First, a suitable starting solution is chosen. Often, this solution is close to the lower detection limit. Then, the potential change is measured caused by increase in the target ion activity by an increment Δa_I. Next, the ISE is placed back into an identical starting solution, and interfering ions are added until the same potential change is registered. The selectivity coefficient is then calculated as the ratio of the respective activity increments resulting in the same potential change:

$$K_{\mathrm{IJ}} = \frac{\Delta a_I}{\Delta a_J} \tag{3.14}$$

On the one hand, the MPM allows for artificial circumventing non-Nernstian slopes and the differences between the charges of the ions in question. On the other hand, lacking theoretical background, the K_{IJ} value obtained by the MPM also lacks predictive ability about the EMF measured with solutions other than those for which it was determined [8–10]. Therefore, the MPM method is practically not in use anymore.

3.3.4 Unbiased Selectivity and the Bakker Protocol

The selectivity coefficients of ISEs with various types of membranes (glass, crystalline, or polymeric) depend on the measurement conditions, in the first place,

on the concentrations of the ions in solutions. Different hypothesis have been proposed to explain this non-constancy [11]. A fundamental reason can be a non-adequacy of simple equations, like the Nikolsky equation, for the description of the electrode potentials in mixed solutions. Indeed, the simplifications used in the derivations of these equations may depreciate the final mathematical forms [12, 13]. There are also experimental sources for the variation of the selectivity coefficients. The point is that the ion exchange at the membrane/solution interface causes small deviations of the composition of the solution in the vicinity of the membrane when compared with the composition of the solution in the bulk [11]. Let us consider first the measurements of the selectivity coefficients by the separate solutions method. The method suggests that the ISE selective to I^{z_I} ions is immersed into a pure solution containing J^{z_J} ions. In reality, the latter solution is a pure electrolyte only in the bulk, while in the vicinity of the ISE membrane, the solution is slightly depleted in J^{z_J} ions and slightly enriched in I^{z_I} ions, because of the ion-exchange process at the membrane/solution interface. Thus, the membrane is effectively in contact with a mixed solution. The more selective is the ISE to the respective I^{z_I} primary ions, the bigger is the impact from these "extra" ions to the membrane potential. This is why the variability of the selectivity coefficients is more pronounced when J^{z_J} interfering ions are highly discriminated by the membrane, while in the case of only moderate selectivity, the K_{IJ} values may be roughly constant.

If the selectivity is quantified by means of the mixed solution method, the whole pattern is pretty much the same. The I^{z_I} primary ions coming from the membrane to the solution slightly increase the values of a_I^{surf}—the primary ions activity in the vicinity of the membrane surface, when compared with a_I—the respective bulk values. The effect intensifies in solutions diluted with respect to the I^{z_I} primary ions.

For ISEs with solvent-polymeric membranes, there is an additional reason for the variability of the selectivity coefficients. Such membranes produce I^{z_I} primary ions and thus contaminate the solutions not only due to the ion-exchange processes, but also due to the trans-membrane flux of ions from the internal solution of the ISE to the sample or calibrator. This effect was proved to determine also the lower detection limit of ISEs in pure solutions [3, 14, 15], see Sect. 7.2.

Thus, the classical methods of the measurements of the selectivity coefficients deliver values biased by the consequences of the ion-exchange processes at the membrane/solution interface and of trans-membrane fluxes of ions. On the basis of this conclusion, Bakker proposed a method of measurements of the so-called *unbiased selectivity coefficients*, also called the *Bakker protocol* [16, 17]. The method suggests using membranes not containing the primary ions. For instance, for K^+ electrodes instead of using the most common cation-exchanger potassium tetrakis(p-Cl-phenyl)borate, one has to use the respective sodium or lithium salt. The measurements must be done in two stages, utilizing two sets of the respective replica electrodes with the membranes of the same composition. The procedure is illustrated by Fig. 3.8.

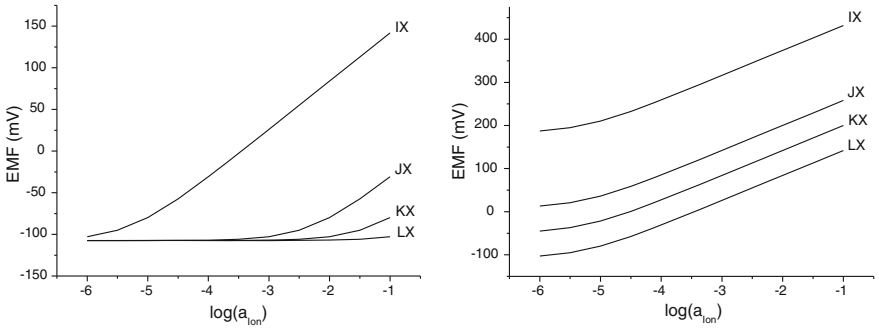

Fig. 3.8 Unbiased selectivity measurements of the selectivity coefficients to I^+ primary ion over J^+, K^+, and L^+ interferences, first stage (*left*), and second stage (*right*). The curves refer to the following values of the selectivity coefficients: $K_{IJ} = 10^{-3}$, $K_{IK} = 10^{-4}$, $K_{IL} = 10^{-5}$. The lower detection limit is $\log a_I = -5.3$. Notice the difference in the EMF scales in the *left* and *right* plots

The left plot in the figure represents the first stage of the Bakker protocol: the traditional SSM measurements of the selectivity. This stage provides with the order of ions arranged according to their interference with the response to the primary target analyte—from strongly interfering to highly discriminated ions. As one can see, even in JX solutions, in those containing J^+ ion, which shows relatively strong interference: $K_{IJ} = 10^{-3}$, the response is strongly nonlinear, and there is practically no response to more discriminated ions: K^+ and L^+. However, one can clearly see the selectivity sequence:

$$I^+ > J^+ > K^+ > L^+$$

Thus, on the second stage, replica electrodes with the same kind of membranes, not being in contact with the primary ions, are filled with LX solution containing L^+—the most discriminated ion. Next, calibrations are performed in other electrolytes from most discriminated to most interfering and, finally, in solutions containing the primary ions. Under this protocol, neither the trans-membrane flux, nor the ion exchange at the membrane/solution interface distort the ISE potential, and one can obtain calibration curves shown in Fig. 3.8, right plot. The curves show Nernstian slopes and the selectivity coefficient values not dependent on the ions concentrations. Furthermore, the selectivity coefficients obtained in accordance with the Bakker protocol are consistent with the respective thermodynamic parameters characterizing the affinity of the competing ions to the aqueous phase and to the membrane phase: the ionic distribution coefficients, the ion-to-ionophore complex formation constants, etc. [17].

3.4 Response Time

The practical response time of an ISE shows how fast the steady value of the EMF is established when the previous sample or calibrator is replaced with the next one. This characteristic is of great importance since it determines the throughput of a measuring device having an ISE as sensor. Therefore, the response time of a novel ISE is normally specified by the inventor. In early days of the ISE research, a lot of work has been done to study the regularities of the response time [7, 18–21]. Also, the term was defined more exactly, for instance, τ_{90}, τ_{95}, the times sufficient for, respectively, 90 or 95 % of the full potential change. Without these specifications, the random noise of the potential hinders the measurements of the response time, since, due to the noise, the readings are never ideally steady. This idea is illustrated by Fig. 3.9.

The curve refers to a flow through K^+ ISE with valinomycin in the membrane, filled with 0.01 M KCl, with Ag/AgCl internal electrode. The EMF is measured against Ag/AgCl electrode in 3 M KCl. The initial solution was 0.1 M KCl. At time 220 s, the flow cell was emptied with an air bubble passed using a syringe and then filled with 0.01 M KCl, also using a syringe. These manipulations took 10 s and caused overshot in the response curve. The ISE potential reached 95 % of the signal change at time 305 s, and the full change was reached at about 350 s. Thus, in this example, $\tau_{95} \approx 45$ s, the "total" response time was even longer: about 90 s. Similar times refer to the back process: from 0.01 to 0.1 M KCl. However, large impact to these times comes from the procedure of replacement of the solution, use of faster diluting/concentrating devices results in $\tau_{95} \leq 5$ s. Furthermore, already in

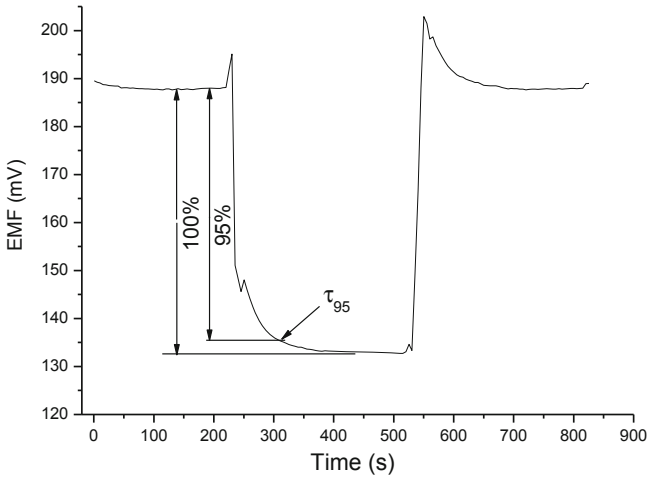

Fig. 3.9 Response curve of a K^+-ISE when 0.1 M KCl is replaced with 0.01 M KCl, and then back with 0.1 M KCl

late 1980s, it was shown that using special devices for very fast sample change allows obtaining the ISE response time in millisecond range [21].

Theories developed in [7, 18–21] considered various processes determining the response time: (1) electrochemical reaction at the membrane/solution interface, (2) diffusion within the membrane phase, and (3) diffusion of the electrolytes across the so-called stagnant layer in the aqueous phase in the vicinity of the membrane.

The practical response time therefore does not tell how fast the interfacial equilibrium is established. The latter process depends on the exchange current densities at the membrane/solution interface and the double-layer capacitance. Electrochemical impedance studies of glass and crystalline membranes showed very fast charge transfer processes [22]. For ionophore-based membranes, the exchange current densities are 10^{-5} A/cm^2 and higher, while the double-layer capacitance is about 10^{-7} F/cm^2, thus giving τ_{RC}—the time constant not more than 0.01 s [23, 24]. The full establishing of the electrochemical equilibrium at the membrane/solution interface takes therefore $t_{eqilibr} = 5\tau_{RC} \leq 0.05$ s. Of course, for a "bad" electrode, it may take much more time to reach the interfacial equilibrium.

Diffusion of ions within the membrane phase takes place within the transient part of the response—when the ISE loses the response to its primary ion in favor of the interference. Therefore, within the linear part of the response, the diffusion of the electrolytes across the "stagnant" layer is the major factor of the response time. Thus, generally speaking, the practical response time of a "good" electrode is determined by the hydrodynamic conditions in the cell when one solution is replaced with another one. Stirring helps obtaining shorter response times.

Long-term kinetics like that studied by Belyustin for glass electrodes does rely on the processes deep in the glass membrane phase [25, 26]. However, this long-term kinetics happens within days and weeks and does not alter practical response time of ISEs.

3.5 Stability and Piece-to-Piece Reproducibility of the ISE Response

Measurements with ISEs rely on calibration. Drift of an ISE readings immersed in the same sample over time suggests that either the standard potential (E^0) or the slope (S) obtained during the calibration cannot be used for the converting of the measured EMF into the analyte activity (or concentration). Thus, insufficient stability of the ISE response puts its practical usefulness under question.

Normally, the slope is much more stable over time than the standard potential. The change of the slope is mostly regular: slow decrease over the ISE lifetime, because of slow leaching of ionophores from membrane to aqueous solutions [27, 28].

For the ISEs with solvent-polymeric ionophore-based membranes, the slope, normally, changes gradually from its initial near-Nernstian value of ±(57–58) or

±(26–27) mV/log a_I (for monovalent or divalent ions, respectively, "+" for cations and "−" for anions), down to ±(50–52) or ±(22–24) mV/log a_I during several months, up to one year, thus determining the ISE lifetime. However, there are examples of ionophore-based membranes with lifetime of several years [29]. The lifetime of crystalline and glass electrodes, if properly handled, is practically non-limited, and the slope does not change over time.

The membrane potential is non-zero only if there is some asymmetry in the system: either the solutions on the two sides of the membrane are not the same or the membrane itself is non-uniform. Good, commercially available electrodes have no "frozen" gradients across membranes and show only negligible asymmetry potential. Therefore, the potential of such a conventional ISE immersed into a solution of composition same as that of the internal filling equals the potential of the internal electrode versus the reference electrode used for the measurements. For instance, an ISE filled with 0.01 M KCl and equipped with Ag/AgCl internal electrode, when immersed into 0.01 M KCl shows about 135–138 mV versus Ag/AgCl reference electrode in 3 M KCl. This value is simply the EMF of a cell comprising Ag/AgCl electrode in 0.01 M KCl versus the same reference electrode. Therefore, ISE membranes themselves impact to the E^0 drifts only if become non-uniform during use. This may happen because of sorption of some undesirable species by the membrane surface or deeper—into the outer layers of membrane. Otherwise, the stability of the E^0 of the conventional ISEs with an internal filling solution (most often, a suitable chloride salt, for example, KCl in K^+-ISEs and NaCl in Na^+-ISEs) and an internal electrode (most often—Ag/AgCl) depends primarily on the constancy of the internal filling composition. Therefore, large ISEs with the internal filling volume of 1–3 ml are typically more stable over time than small ones with only 0.1–0.2 ml of the internal solution. Water mostly leaves the internal solution due to evaporation if the ISE is not hermetically closed. In the case of solvent-polymeric membranes, also a trans-membrane diffusion of water is possible, either from the internal solution to sample or vice versa—dependent on the difference in water activities in the respective solutions. Although this effect is small, it sometimes may impact to the instability of the standard potential. Some impurities present in samples may diffuse across the membrane from sample to the internal solution and accumulate there, causing significant drifts of the E^0. For instance, even small flux of Br^- or I^- ions across an ISE membrane (so small that it does not deteriorate the ISE slope) may cause a significant change of the E^0 due to the change of the internal Ag/AgCl electrode potential in the presence of these ions. Obviously, these diffusion-induced effects happen only with ISEs with solvent-polymeric membranes and do not happen with crystalline and glass ISEs. On the other hand, the latter two types of ISEs are more sensitive to the adsorption on the membrane surface and formation of surface oxide layers. Therefore, glass and crystalline ISEs require refreshment of the membrane surface, by etching or polishing, respectively.

From the practical point of view, it is advisable to replace the internal solution with a fresh portion every two weeks or more often dependent on the volume of the internal solution and on how tight the electrode is closed up. Then, the E^0 value

or, rather, the potential in a certain "control" solution remains virtually the same (±0.5 mV) during the whole lifetime of the ISE.

In various special devices, like in clinical analyzers, the changes of the E^0 are compensated by the measurements procedure. The reliability of the data is guaranteed by measuring the potential in a certain control solution after every three samples, or even after each sample—if this is required. For more details about ISEs in clinical analyzers, see Sect. 8.4.

The solid-contact electrodes, those without internal filling, intrinsically, are better suited for high stability of the standard potential over time. Indeed, the solid-contact ISEs with glass and crystalline membranes show excellent stability over time [30, 31]. However, for ISEs with ionophore-based membranes, securing a good stability of the E^0 remains a challenging task [32, 33]. For more details, see Sect. 8.2.

The piece-to-piece reproducibility of the ISE potentials is not an issue for a user having only one electrode. However, for a scientists or a manufacturer, a poor piece-to-piece reproducibility indicates some problem with electrodes. Piece-to-piece reproducibility is also important when ISEs are used for in-line monitoring of an industrial process. Then, it may be critical to replace a malfunctioning sensor with a new one without wasting time for calibration. For this task, it is critical to have the same values of the ISE calibration parameters: the standard potential and slope.

Conventional ISEs with internal filling solution and internal electrode show piece-to-piece reproducibility of the standard potential of about ±1 mV and better, the piece-to-piece reproducibility of the slope is about ±0.2 mV. Solid-contact ISEs with glass and crystalline membranes also show excellent piece-to-piece reproducibility. For solid-contact glass electrodes with Li-Sn alloy as the internal system, it is even possible to use "factory calibration" which remains stable for several years [30]. Unfortunately, the piece-to-piece reproducibility of solid-contact ISEs with polymeric membranes with ionophores, so far, does not allow replacing one electrode with a replica one without calibration. Although slope values within a batch of ISEs normally vary within the same narrow range of ±0.2 mV, the standard potentials may deviate from one another in ±15 mV or even more.

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