Chapter 7
Modern Trends in the ISEs Theory and Applications

This chapter relates to four modern but already well-developed areas in ISEs: real time and space modeling, trace analysis, ISEs under nonzero current, and electronic tongue. Novel materials used in ISEs are discussed in the respective chapters.

7.1 Real Time and Space Modeling of ISEs

The multispecies approximation described in Sect. 4.2.5 was among the first approaches to develop ISE theories using computer simulations of the membrane potential. The multispecies approach is limited to a quasi-steady state of the membrane, see Sect. 4.2.5.

More recently, a number of attempts have been made aimed at description of the membrane potential in the real time and space. Morf invented a model describing the propagation of ions within an ionophore-based membrane [1]. This description does not account for the non-compensated charges in the double layer at the interface.

More advanced theory is developed in Lewenstam' group [2–7]. This theory does not rely on equilibrium nor on steady state. The core of the Lewenstam' theory is the numerical solution of the system of the Nernst–Planck and the Poisson equations:

$$J_k(x,t) = -D_k\left[\frac{\partial C_k(x,t)}{\partial x} - z_k C_k(x,t)\frac{F}{RT}E(x,t)\right] \tag{7.1}$$

$$I(t) = F\sum_k z_k J_k(x,t) + \varepsilon\frac{\partial E(x,t)}{\partial t} \tag{7.2}$$

Equation (7.1) describes $J_k(x,t)$ the place (x) and time (t)-dependent flux of the species k as a function of D_k, $C_k(x,t)$ and $E(x,t)$,—the diffusion coefficient, the species concentration, and the electric field. In Eq. (7.2), the Poisson equation rewritten for $I(t)$ the time-dependent total current density, z_k stands for the species charge and ε for the dielectric permittivity. This allows for tracing the formation of

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the boundary and the diffusion potentials in membranes over time and space. Furthermore, the theory provides with guidelines for the optimization of the membrane and of the internal solution compositions for the improvement of the ISE sensitivity. In this way, the theory is applied for the optimization of the membrane and of the internal solution compositions of ISEs for trace analysis (see Sect. 7.2) [6, 7]. The comparative review of different theoretical descriptions of the ISE membrane potential and selectivity is given in [8].

On the other hand, even this very much advanced theory describes the membrane as an ideal system: the species concentration is used instead of activity, the diffusion coefficients are assumed constant, and no local changes of the dielectric permittivity (e.g., close to the interface) are discussed. Furthermore, these advanced theories assume the electrolytes in membranes fully dissociated. Therefore, the effects of the association with membranes, so far, are treated only on the basis of the multispecies approximation described in Sect. 4.5.3.

7.2 ISEs in Trace Analysis

For a long time, ISEs could not be used for the measurements at concentrations below 10^{-5}, at best below 10^{-6} M. The decisive step in the understanding of the nature of the lower detection limit of ISEs, and of what can be done to improve it, was made by Sokalski and co-workers [9]. After this pioneering work describing large improvement of the low detection limit of ISEs with ionophore-based membranes studies aimed at potentiometric measurements in sub-nanomolar concentration range became a mainstream of the ISE research. Deviations from Nernstian response of ISEs in micromolar and sub-micromolar concentration range are caused by the local increase in the concentration of the analyte in the sample in the vicinity of the sensor membrane, see Fig. 7.1. It is now generally recognized that this local increase in the analyte concentration is caused by trans-membrane fluxes of ions co-extracted from the internal filling solution to the sample and by the fluxes caused by the replacement of the primary ions in the membrane with the interfering ions due to ion exchange [10–12]. These fluxes have been registered experimentally by the electrochemical scanning microscopy method [13]. The internal reference system of a solid contact ISE, for example, based on a conducting polymer also may be a source of analyte ions which eventually contaminate sample solutions, although to somewhat lesser extent than in the case of ISEs with internal aqueous solution [14–17].

The resulting deviation is insignificant if the bulk concentration of the sample is larger than the impact from the trans-membrane flux. With dilution, the deviation increases, and at sample concentrations below 10^{-5} M, the ions brought by the trans-membrane flux determine the surface concentration of the analyte.

The driving force for these fluxes are large differences in the activities of the target analyte in diluted samples and in internal solutions containing analyte ions in millimolar concentration or at even higher level. The first approach aimed at

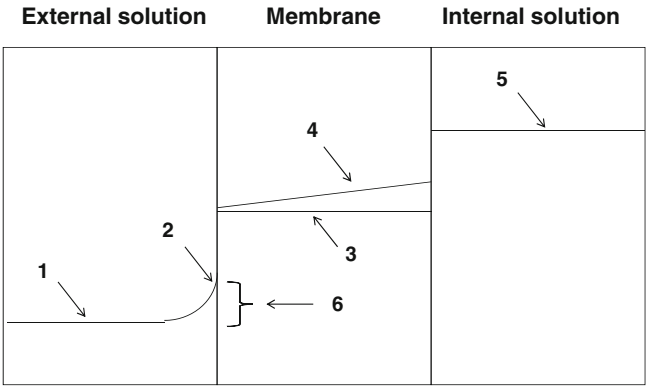

Fig. 7.1 Schematic representation of the electrolyte profiles in a membrane/solution system. (*1*) The electrolyte concentration in the sample bulk; (*2*) the electrolyte concentration in the vicinity of the membrane; (*3*) the "ideal" flat analyte ion concentration profile determined by the ion-exchanger concentration; (*4*) the real analyte ion profile (caused by the co-extraction); (*5*) the electrolyte concentration in the internal solution; (*6*) the deviation of the surface concentration of the analyte from its bulk value

reduction in the trans-membrane fluxes was invented in the late 1990s [9]. It relied on maintaining the activity of the target analyte in the internal filling solution of an ISE at a very low level by means of a suitable buffer while maintaining also a sufficiently high activity of an interfering ion. Under these conditions, the analyte ions in the ISE membrane layers close to the internal surface are largely replaced by the interference, producing a gradient of the concentration of the analyte ions across the membrane. This gradient, ideally, eliminates ion fluxes directed to the sample and in this way ensures Nernstian response of the ISE down to very low concentrations. If no suitable buffer exists, low activity of analyte in the internal solution may be kept by using, for example, ion-exchange resins [18, 19].

The disadvantage of this (chemical) approach is that the trans-membrane fluxes of ions are eliminated, rigorously speaking, at only one concentration of the analyte in the sample. From the practical view point, this means that the slope in even more diluted solutions is super-Nernstian because then the flux is directed toward the internal solution and the sample in the vicinity of the membrane is depleted of the analyte ions (see also Fig. 3.3).

More advanced approaches are based on the theory of diffusion and suggest modifications in the membrane geometry or composition [20]. The magnitude of the trans-membrane flux can be decreased by lowering the respective driving force: the gradient of the analyte ion concentration, using therefore thicker membranes [21, 22]. Also, the flux can be decreased by reducing ion diffusion coefficients, that is, by higher content of polymer in the membrane [23]. Transportation of ions across membranes can be also minimized by means of dispersing of silica gel microparticles in the membrane [24]. This is how the deviations from Nernstian response in diluted samples can be minimized at the cost of increasing the sensor

resistance. Also, when microparticles are incorporated, membranes show some loss of selectivity [23]. The acceleration of the ion transport in the sample phase can be achieved using rotating disc electrode (the electrode rotates during experiments inducing a flux of analyte to the electrode) or simply by stirring [25]. Variety of these approaches was critically analyzed and evaluated [12].

An alternative way of the elimination of the trans-membrane fluxes (or, rather, of the consequences of these fluxes) is based on galvanostatic polarization of the ISE. This (electrochemical) approach has been first proposed by Buck [26], and since then, it was utilized by several groups of researchers [15, 16, 27–30]. By applying a suitable current, one can eliminate the trans-membrane ion flux. Galvanostatic polarization seems to be more flexible approach aimed at the improvement of the low detection limit, when compared with the modification of the composition of the internal solution, or of the composition and/or the geometry of the membrane.

When the analyte concentration in the sample is below 10^{-5} M, the gradient of the analyte ion concentration across the membrane is determined by the concentration of the internal electrolyte which is, typically, 10^{-3} M or higher. Therefore, the steady trans-membrane flux across the membrane to solutions with concentrations of 10^{-5} M or lower is also the same. In turn, the steady electric current compensating this flux must be the same [28]. However, waiting for the steady state may take several hours and therefore is not practical. If the steady state is not reached, then for each particular concentration of the analyte a particular, specific compensating current is needed. This is why the galvanostatic polarization using a certain constant current density works ideally only in a very narrow concentration range. Outside this range, a sub- or a super-Nernstian slope is registered, similarly to chemical approach which relies on buffering the internal solution. Therefore, obtaining linear Nernstian response in a broad concentration range in practically acceptable time requires specific compensating current magnitudes tuned for particular concentrations of the analyte in the sample.

Tuned galvanostatic polarization has been successively used by Mikhelson et al. first for Ca^{2+} electrodes [31] and later also for Cd^{2+} electrodes [32] with PVC membranes containing neutral ionophores. The polarizing current density was optimized for each concentration of the analyte ion, see Fig. 7.2. The ISEs were polarized for certain time (always the same). The potential value registered in 0.2 s after the current is turned off was used as the analytical signal (plotted in Fig. 7.2, curve 2). The same approach helped enlarging the working range of Pb^{2+} ISE with crystalline membrane [33]. Since the optimal density of the compensating current is dependent on the analyte concentration, it is known only for calibrators, but not known for samples. This problem was successfully solved on the basis of the regularities governing the relation between the analyte concentration in sample and the respective optimal current density revealed in [31, 32]. It was shown that the optimal current density is proportional to the delta of the logs of the analyte ion activity in the sample in question and that at the lower detection limit:

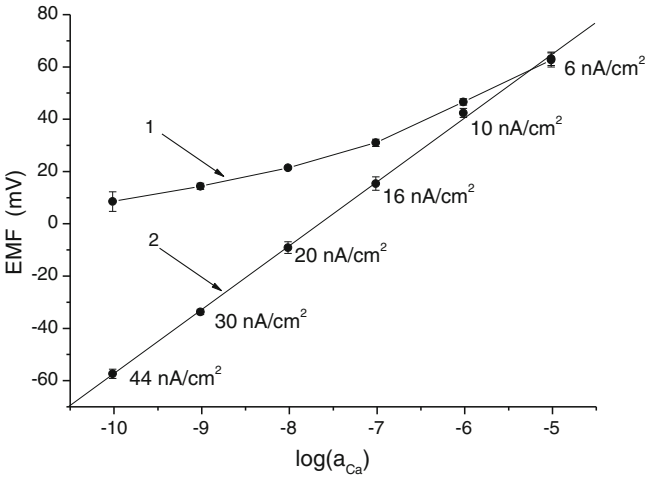

Fig. 7.2 Data obtained for Ca ISE based on the ionophore ETH 1001. Traditional zero current calibration plot (*1*) and calibration plot of electrodes polarized with optimized currents (*2*) [31]. Adapted with permission from Peshkova et al. [31]. Copyright 2008 American Chemical Society

$$i_{\text{opt}} = \beta\left(\log a_I - \log a_I^{\text{LDL}}\right) \tag{7.3}$$

Two practically feasible procedures which deliver both the optimal current density and the analyte ion concentration have been proposed and gave good results [31–33].

7.3 Use of ISEs Under Nonzero Current Conditions

Improvement of the lower detection limit is not the only area where ISEs are used under nonzero current conditions. Ionophores are widely used in voltammetric [34–36], conductometric [34, 37, 38], and optical sensors [39–41]. This suggests that the chemical interactions which provide a basis for the response of these different sensors do not require the traditional (for ISEs) limitation: measurements under zero current. For decades, polarization of ISEs was widely used for studying the mechanism of the response [42–45]. However, except of a few works by Nieman with fluoride mono-crystalline and calcium polymeric electrodes [46–49], polarization was never used to improve the analytical behavior of ISEs. Nieman made a rapid series of current measurements at various voltage pulse magnitudes (0–5 V) lasting 100 μs and then extrapolated the current–voltage curve to zero voltage. According to Nieman, the measured signal is concentration rather than activity dependent, making adjustment of the ionic strength unnecessary. This idea did not get further development. The situation changed drastically in the late 1990s

when they started using galvanostatically polarized ISEs for trace analysis (see Sect. 7.2).

Another promising area of polarized ISEs refers to the modification of the type of the electrode response (cationic or anionic) and that of the selectivity. Basically, the type of the ISE response and the selectivity are determined by the membrane composition. Shvarev found that when an ISE is under nonzero current conditions, it is possible to impose a certain type of the response and also modify the selectivity by passing current across the electrode membrane [50]. This can be done with ISEs having membranes with neutral ionophores and lipophilic background electrolyte (e.g., tetradodecyl ammonium tetrakis(p-Cl-phenyl) borate), but without ion-exchanger sites [50]. The concentration of the analyte ion in the membrane is when adjusted by passing current of a tuned density for a certain time. Polarization of a membrane containing Na^+-selective neutral ionophore Na-X (see Sect. 4.2) with low cathodic current: about -3 mcA/cm^2 results in pseudo-Nernstian response to Na^+ ions with the selectivity coefficient determined by the ionic partition coefficients and ion-to-ionophore complexation constants:

$$K_{\mathrm{NaK}} = \frac{k_K}{k_{\mathrm{Na}}} \frac{K_{\mathrm{KL}}}{K_{\mathrm{NaL}}} \tag{7.4}$$

When the electrode is polarized with cathodic current of higher density (approx. -30 mcA/cm^2), the concentration of the extracted ions exceeds the ionophore content, and the selectivity is determined by ionic partition coefficients only, like in the case of an ionophore-free membrane:

$$K_{\mathrm{NaK}} = \frac{k_K}{k_{\mathrm{Na}}} \tag{7.5}$$

The change of the sign of the current allows replacing a cationic response with anionic. As shown in [50], use of small anodic current (about +3 mcA/cm^2) results in a response to Cl^- anions.

Nonzero current measurements are also suitable for sensing polyions, for example, heparin ($z \approx -70$) and protamine ($z \approx 20$). The classical equilibrium measurements do not allow sensing these ions because the large denominator in RT/zF—the Nernst factor, results in negligible slope. Therefore, Meyerhoff invented a non-equilibrium procedure of measurements when the process is under the diffusion control, and the potential difference upon addition of Y^- polyionic analyte obeys equation below [51–53]:

$$\Delta E = \frac{\mathrm{RT}}{F} \ln\left(1 - \frac{z_Y D_{\mathrm{aq}} \delta_m}{C_R D_m \delta_{\mathrm{aq}}} C_Y\right) \tag{7.6}$$

Here, z_Y is the charge of species Y^-, C_Y is its concentration in the sample, C_R is the concentration of R^+ ion-exchanger sites in the membrane, D_{aq} and D_m are the ion diffusion coefficients in the aqueous phase and in the membrane phase, δ_{aq} and δ_m are the thicknesses of the diffusion layers in these phases.

The linearity and the reproducibility of the response of ISEs under diffusional control were poor [51–53]. However, applying alternating galvanostatic and potentiostatic pulses allowed obtaining very good reproducibility of the response to polyions. Furthermore, the calibration curve was linear with the slope like for a monovalent ion [54]:

$$E = \frac{\mathrm{RT}}{F} \ln\ C_Y \tag{7.7}$$

Nonzero current measurements provide therefore with new opportunities also for polyion sensing.

7.4 Multisensor Arrays, Electronic Tongue

The variability of the traditionally measured selectivity coefficients hinders correction for interferences even in artificial mixed solutions containing only a handful of ions. The use of the unbiased selectivity coefficients requires special protocols which are difficult to follow dealing with real samples. Therefore, for real samples, the correction of the data for un-sufficient selectivity of electrodes is even more challenging, and hardly feasible at all.

An alternative approach may help solving this problem. This approach relies on measurements with arrays of sensors having moderate selectivity and processing the data with chemometrical methods.

Initially, the studies concentrated on the imitation of the functioning of the olfaction organs of mammals [55]. Attempts of development of the so-called *electronic nose* started in early 1980s [56]. These systems are nowadays widely used for the analysis of multicomponent gas mixtures [55].

In analogy to the electronic nose, the respective systems for the analysis of liquid samples (described first in [57]) are called *electronic tongue* [57–59]. In contrast to the traditional approach when attempts are made to use sensors with as highest selectivity as possible, the electronic tongue system relies on sensors with only moderate selectivity and having the so-called cross-sensitivity. In this way, each sensor in the array, in principle, delivers information on the concentrations of a number of analytes. The next step is to decode the signals obtained from the sensor array.

The sensors in the array can be of different nature—not necessarily ISEs. However, studies with ISEs were, probably, most successful, and therefore ISEs predominate among various types of sensors used for the electronic tongue systems [60–62]. In turn, although different types of ISEs can be utilized in electronic tongue, electrodes with chalcogenide glass membranes (see Sect. 6.4) are particularly suitable for these devices.

The number of sensors in the array can vary, but most typical number is about 10–20. In contrast to the classical measurements with ISEs, the electronic tongue system can work without a reference electrode. In such a setup, the potential

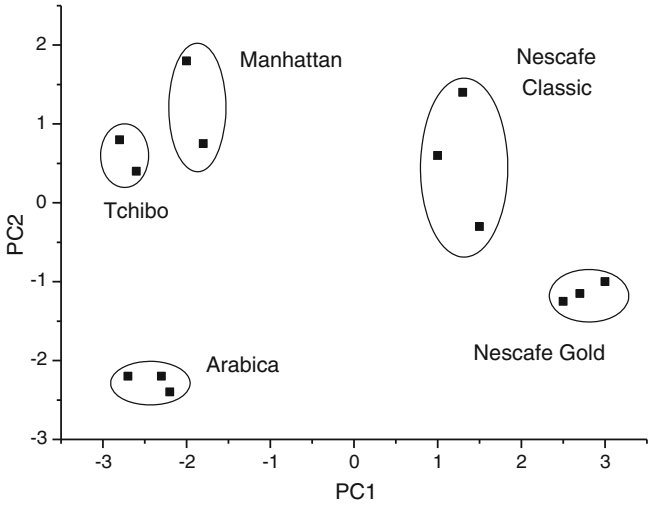

Fig. 7.3 Principal component plot identifying different sorts of coffee based on analysis with electronic tongue [67]. Adapted with permission from Legin et al. [59] Copyright 1997 Elsevier

difference is measured for all pairs of the electrodes in the array [63]. This is advantageous since reference electrodes often cause problems with the measurements.

The signals obtained from the sensor array are processed using various chemometrical methods: multilinear and nonlinear regressions, partial least squares, artificial neural networks [64]. The interpretation and representation of the data is often based on the principal component analysis method. This allows for the characterization of the samples not only in terms of the concentrations of the particular analytes, but also for the recognition of the nature of the sample: different types of samples fall into different places in the principal components plot. In this way, it is possible to distinguish between different sorts of juices [59, 65], mineral waters [66], coffee [67], tea [68], milk and dairy products [69, 70]. Example of identification of various sorts of coffee using electronic tongue and processing the data with artificial neural network is shown in Fig. 7.3. Electronic tongue is successfully used in a number of clinical applications: in artificial kidney [71, 72], in blood [73], and in urine analysis [74].

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