AC-Impedance Studies of Ion Transfer Across Ionophore-Based Ion-Selective Membranes

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Fundamental complexities related to the studies on interfacial charge transfer at ionophore-based ion-selective electrode (ISE) membranes have been briefly discussed. The presented data obtained from ac-impedance studies on ISEs selective to K⁺, Na⁺, Li⁺, and Ca²⁺ ions have shown fast interfacial transfer of primary ions, and also of interfering ions, supporting the concept of fast establishment of interfacial electrochemical equilibrium towards all competing ions in the solution.

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Ionophore-based ion-selective electrodes (ISEs) constitute a well-developed class of potentiometric chemical sensors, widely used in analytical practice [1]. Potentiometric response of good ISE is fast, close to Nernstian, and stable in time. The prerequisite for fast and stable Nernstian response is fast establishment of electrochemical equilibrium at the interface between the ISE membrane and the sample phase. Normally, it is assumed that all competing ions are at equilibrium at the interface, and selectivity of the potentiometric response is governed by equilibrium properties of membranes [2]. Alternative (kinetic) approach assumes mixed potential response, so that at least discriminated ions may be not at equilibrium at the interface, see Cammann [3].

From the R&D point of view, the issue whether the interface is at equilibrium towards all the competing ions, or to only some of them (or to none of them) is important. In case of equilibrium, selectivity of the response is governed (primarily) by the ratios of ion-to-ionophore complexation constants for the competing ions, whereas the value of mixed potential is related to the ratio of the exchange current densities of ions. Thus, the development of novel ionophores may be focused either at selective complexation, or at selective lowering of the interfacial charge transfer barrier (activation energy).

Recent developments related to lowering the detection limits of ISEs, have evoked a new question concerning the kinetics of the interfacial charge transfer. It is already well established that tailoring the composition of the internal solution (Sokalski et al. [4]) of ISE is not the only method to improve lower detection limit. In fact, galvanostatic polarization of the ISE membrane appears to be even more effective, and definitely a more flexible approach aimed at the improvement of the dynamic range of ISE [5, 6, 7]. The passing current allows one to adjust trans-membrane ion fluxes in such a way that ions from the membrane do not contaminate the sample. Obviously, this approach works only if the interface remains at equilibrium, although the activities of potential-determining species at the interface are affected by migration and therefore are different from the values at the zero current.

Recently introduced Nernst-Planck-Poisson model, see Sokalski et al. [8, 9], which appears to be a breakthrough in the theory of trans-membrane charge transfer, strongly demands on the data on the kinetics of the interfacial processes, thus establishing additional interest in this knowledge.

In this work, I have discussed some methodological issues which must be kept in mind when studying electrochemical properties of aqueous/nonaqueous interfaces. Also, a brief selection of the data related to the charge transfer across ISE membrane/solution interface and scattered in different journals has been presented.
METHODOLOGICAL ISSUES OF INTERFACIAL CHARGE TRANSFER STUDIES

Fundamental complexities of membrane/solution interfaces

It is widely recognized that studies on the kinetics of ion transfer across ISE membrane/solution interface are hampered by high ohmic resistance of the membrane bulk, which is connected in series with the interfacial resistance. Due to this reason, reliable measurement of this relatively low interfacial resistance is a challenging experimental task. There are, however, some fundamental issues which make the interpretation of the experimentally obtained results difficult.

An ISE membrane/aqueous solution interface is a special type of an interface between two immiscible electrolyte solutions (ITIES). ITIES have been intensively studied since 1970s, see the reviews of Koryta [10], Buck et al. [11], Vanysek [12]. These works have mainly addressed the equilibrium parameters of ITIES. Consistent scales were developed for free energies of the interfacial ion transfer between aqueous and nonaqueous solutions, see Koryta [10], Koczorowski et al. [13], and Kakiuchi et al. [14]. These values characterize the affinity of ions towards aqueous and organic phases, being therefore very useful for interpretation of potentiometric selectivity of ISEs. Further studies carried out mostly by cyclic voltammetry and polarography provided more data on the stoichiometry and stability of ion-to-ionophore complexes in organic phases, including ISE membranes, see Wilke et al. [15], Samec et al. [16], Takeda et al. [17].

Turning now to the interfacial kinetics at ITIES, let’s state first that one should be very careful with the interpretation of the data related to the interfacial kinetics, even if these data are reliable from experimental point of view. Fortunately, classical relation between the charge transfer resistance and the exchange current density must be valid also for ITIES, [18]. However, charge transfer across ITIES and also across membrane/solution interface is fundamentally different from that across metal/solution interface. In the latter case, even for amalgams, an oxidation-reduction process always takes place. On the contrary, the ions crossing ITIES do not change their oxidation states. Basically, the ions change only their solvation spheres, replacing water molecules with organic solvent molecules, or vice versa. Let’s denote the free activation energy of this process as $\Delta G^*_{\text{solv}}$. Then, according to Girault et al. [19] and Murtomäki et al. [20], fundamentally important parameter for the kinetics at ITIES is the relation between $\Delta G^*_{\text{solv}}$ on one side, and $\Delta G^*_{\text{diff}}$ (free activation energy of ion diffusion) on the other side. Of course, here we mean the $\Delta G^*_{\text{diff}}$ in that of the two contacting phases, where diffusion is more slow. Normally, this is the organic phase. If $\Delta G^*_{\text{solv}} \approx \Delta G^*_{\text{diff}}$ and especially in the case when $\Delta G^*_{\text{solv}} < \Delta G^*_{\text{diff}}$, the interfacial charge transfer is mixed with the diffusion in that of the two phases where
diffusion is slow. In this case, slow reaction can not be revealed experimentally, and the whole process will appear only as transportation. On the other hand, this does not necessarily mean that the interfacial charge transfer proceeds much faster than diffusion, it only means that it is not much slower. This reasoning is illustrated in Figure 1.

![Energy Profile Diagram](image)

**Figure 1.** A scheme of energy profile of the species moving through the aqueous phase, across the aqueous/organic interface, and through the organic phase (or vice versa). Diffusion is shown as a series of activation barriers of equal height in each of the respective phases; higher barriers in the membrane phase refer to slower diffusion. The charge transfer reaction is shown as a sole activation barrier located at the interface. Curve 1 – $\Delta G_{solv,I}^e \gg \Delta G_{diff,I}^e$; interfacial charge transfer appears as slow reaction, and can be revealed experimentally. Curve 2 – $\Delta G_{solv,I}^e \approx \Delta G_{diff,I}^e$; interfacial charge transfer is mixed with slow diffusion, and can be hardly evolved.

Moreover, theoretical considerations have shown that transfer coefficients at ITIES should remain constant only when being close to the equilibrium potentials [21]. This means that an increase of voltage (i.e., in impedance studies) aimed at the improvement of the signal-to-noise ratio can not be advised, giving an additional obstacle to the measurements.

**Interpretation of electrochemical impedance data with Randles equivalent circuit**

Randles equivalent circuit (Fig. 2A) is a predominating case when either ITIES or an ISE membrane is considered in electrical terms. Although these electrical terms are not necessarily ideal resistors and capacitors (e.g., constant phase elements are frequently used instead of capacitors), we must realize that equivalent circuits are...
still very much idealized images of the true electrochemical systems. From this point of view, experimental setup must be as simple as possible to obtain unambiguous conclusions. For instance, it is strongly advisable to use the same solution at both sides of the ISE membrane.

In this symmetric case, Randles circuit presented in Figure 2A is simplified to the circuit shown in Figure 2B, and also the relations between respective parameters are very simple:

\[ R_s = R_f/2, \quad R_{st} = R_c/2, \quad C_{dl} = 2 \times C_{2}, \quad Z_w = Z/2, \quad R_b = R_t, \quad \text{and} \quad C_g = C_1. \]

Another approach is to make one side of the membrane non-polarizable using highly concentrated electrolyte solution. It is, however, difficult to predict in advance the appropriate concentration. Moreover, the membranes being in contact with concentrated solutions may suffer from Donnan’s exclusion failure [22] and transmembrane fluxes of the co-extracted ions may bias the results. From this point of view, early data obtained by Cammann [23] do not seem reliable.

Sometimes, the data on the interfacial charge transfer and double-layer capacitance are extracted from nonidealities in high-frequency semicircle in the impedance spectra, as well as from nonlinearities in the Warburg impedance [24]. However,
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extraction of interfacial parameters from this sort of peculiarities does not seem trustworthy if one bears in mind fundamental complexity of ITIES as compared to metal/solution interface.

To the best of my knowledge, there are only few reports on the impedance spectra with more than one clearly resolved semicircle [25, 26, 27, 28, 29, 30]. Interestingly, not all these data refer to the interfacial charge transfer. Low-frequency semicircles [25, 26] were attributed by the authors to the formation of a thin film at the membrane surface exudates of plasticizer, depleted with respect of ionophores and ions. Low frequency semicircles reported by Ye et al. [29] were attributed to the formation of layers of nonionic detergents adsorbed at the membrane surface.

Geometric capacitance of ISE membranes, which are typically non-polar [31], is expected to be much lower than that of the double layer. This is why it is very often taken for granted that membrane’s bulk is responsible for the formation of a high-frequency semicircle in the impedance spectra, while the interface might be reflected at lower frequencies. Zhang et al. [28] have utilized this reasonable assumption in their study on Mg2+-ISE. It seems advisable, however, to study how the impedance spectra vary with the changes of experimental conditions, e.g. concentration of aqueous solutions. In principal, the semicircle referring to the membrane’s bulk should be independent on the composition of the aqueous solution. On the contrary, the semicircle representing the interface is expected to show a regular dependence on the concentration, with transfer coefficient $\tau$ not too far from 1/2.

SELECTED EXPERIMENTAL RESULTS RELATED TO THE KINETICS AT ISE MEMBRANE/SOLUTION INTERFACE

Below, I briefly discuss some results of the studies on charge transfer across ISE membranes. For more details see the following references [30, 32, 33].

Experimental

Neutral ionophores: valinomycin (Val) for K⁺ ISEs, 4-tert-butylcalix[4]arene (NaX) for Na⁺ ISEs, and (−)-(R,R)-N,N'-Bis[11-(ethoxy-carbonyl)-undecyl]-N,N'-4,5-tetramethyl-3,6-dioxaocan-diamid (ETH 1001) for Ca²⁺ ISEs were of Selectophore grade (Fluka). An Li VIII ionophore – (N,N,N',N,N'N'-Hexacyclohexyl-4,4',4''-propyldyne-tris-(3-oxabutramid) was originally invented by Bochenska et al. [34] and synthesized for us at Gdansk University of Technology. Ionic additives: potassium tetrakis(4-chlorophenyl)borate (KTTPB) and sodium tetrakis(4-fluorophenyl)borate (NaFTPB), solvent plasticizers: bis(2-butylpentyl)adipate (BBPA) and 2-nitrophenyleoctyl ether (nNPOE), poly(vinylchloride) (PVC, high molecular mass) were of Selectophore grade (Fluka). Volatile solvents used were: cyclohexanone (CH) (extra pure, Merck) and tetrahydrofuran (THF) (HPLC grade, Lab-Scan). Inorganic electrolytes: KCl, NaCl,
LiCl, and CaCl₂ were of analytical grade (J.T. Baker). Ultrapure water (ELGA Maxima, 18.2 MΩ·cm resistivity) was used to prepare all aqueous solutions.

The membrane cocktails were prepared by dissolving appropriate amounts of ionophores, ionic additives, plasticizer, and PVC in freshly distilled tetrahydrofuran. The PVC-to-plasticizer ratio was 1 : 2. Dry content in the cocktails was 13–14%. To obtain the membranes, 400 µL of the respective cocktails were poured onto Teflon plates of a diameter of 18 mm, and left to dry overnight. Special attention was paid to avoid fast evaporation of THF. The thickness of membranes was approximately 40 µm in the center and gradually increased up to 300 µm at the edges; the average thickness was 220 µm. The membranes were glued to PVC bodies using a solution of PVC in cyclohexanone. Compositions of the membranes are presented in Table 1.

Table 1. Membrane compositions

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Ionophore*, mmol L⁻¹, %</th>
<th>KCITPB, mmol L⁻¹, %</th>
<th>ETH 5000, mmol L⁻¹, %</th>
<th>Plasticizer, %</th>
<th>PVC, %</th>
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<tbody>
<tr>
<td>K1</td>
<td>16.1, 1.09</td>
<td>10.0, 0.27</td>
<td>10.0, 0.70</td>
<td>BHPA 67.7</td>
<td>30.2</td>
</tr>
<tr>
<td>K2</td>
<td>16.1, 1.10</td>
<td>10.0, 0.28</td>
<td>–</td>
<td>BHPA 68.1</td>
<td>30.5</td>
</tr>
<tr>
<td>Na1</td>
<td>15.0, 1.0</td>
<td>7.5, 0.24</td>
<td>7.5, 0.56</td>
<td>BHPA 65.7</td>
<td>32.5</td>
</tr>
<tr>
<td>Na2</td>
<td>15.0, 1.0</td>
<td>7.5, 0.24</td>
<td>–</td>
<td>BHPA 66.0</td>
<td>32.7</td>
</tr>
<tr>
<td>Ca1</td>
<td>20.9, 0.94</td>
<td>10.0, 0.33</td>
<td>10.0, 0.75</td>
<td>BHPA 65.5</td>
<td>32.5</td>
</tr>
<tr>
<td>Ca2</td>
<td>20.9, 0.94</td>
<td>10.0, 0.33</td>
<td>–</td>
<td>BHPA 66.0</td>
<td>32.7</td>
</tr>
<tr>
<td>Li1</td>
<td>10.0, 0.53</td>
<td>5.0, 0.16</td>
<td>–</td>
<td>BHPA 66.21</td>
<td>33.10</td>
</tr>
<tr>
<td>Li2</td>
<td>10.0, 0.54</td>
<td>–</td>
<td>–</td>
<td>BHPA 66.30</td>
<td>33.16</td>
</tr>
</tbody>
</table>

* Valinomycin for K, Na X for Na, ETH 1001 for Ca, and Li VIII for Li.

Potentiometric measurements were carried out at the room temperature (23 ± 2°C) using the following galvanic cells:

Ag | AgCl | KCl (3 mol L⁻¹) | external solution | membrane | internal solution | AgCl|Ag

Potentiometric response and impedance were measured first in the solutions containing only the discriminated ions and using the respective electrolyte (0.01 mol L⁻¹) as the internal solution. The electrodes were soaked for 2 days in respective solutions before EMF measurements were carried out. After the measurements in the solutions containing the discriminated ions, the electrodes were soaked for 2 days in the solutions containing respective primary ions, and then their responses to these primary ions as well as the impedance spectra were recorded. Afterwards, the measurements were repeated for the discriminated ions.

In potentiometric measurements, the reference electrode was a silver-silver chloride electrode (3 mol L⁻¹ KCl) having a contact with the solution through a bridge filled with 3 mol L⁻¹ KCl. ISEs and the reference electrode were connected to an EMF 16 Interface multichannel millivoltmeter (Lawson Labs, Inc.) controlled via PC for data acquisition. EMF values were averaged from the numbers measured and collected within 5 min. Calibration procedures were performed by sequential dilution using two Metrohm 700 Dosinos controlled via a Metrohm 711 Liquino system. Three identical electrodes of the same membrane composition were used for the investigations.
AC impedance measurements were performed for totally symmetric cells, i.e. the same electrolyte of the same concentration was used as the inner and outer solution. Chlorinated silver wire electrodes (working and reference), and glassy carbon counter electrode were used. A frequency response analyzer (Autolab PGstat 20 FRA 2; Eco Chemie) served for impedance measurements. The spectra were recorded within a frequency range 100 kHz–0.01 Hz applying a sinusoidal excitation signal of the amplitude ±5 mV. The impedance data were analyzed applying the fitting program available within Autolab software.

Potentiometric and impedance measurements were carried out in the electrolyte concentration range: $10^{-3}$–$10^{-1}$ mol L$^{-1}$. The beakers and the reference electrode bridge were made of plastic to prevent contamination of the samples with ions from glass.

Results and Discussion

It is very well known that ISEs lose the response towards the discriminated ions after the membrane is contacted with the respective primary ions. One of the reasons for this loss is contamination of the samples with primary ions from the membranes. Another potential reason is slow charge transfer of discriminated ions when the membrane is converted to the form of the primary ion. There is a hypothesis that neutral ionophores bounded to primary ions may inhibit the transfer of discriminated ions. I have addressed this issue studying ISEs selective to K$^+$, Na$^+$, Ca$^{2+}$, and Li$^+$. Most of the membranes under study included the respective neutral ionophore, and also a suitable ion-exchanger (Tab. 1). In case of Na$^+$, Ca$^{2+}$, and Li$^+$ ISE membranes, KCITPB was used as the ion-exchanger, while in case of K$^+$ ISE one used NaFTPB. Accordingly, none of the membranes contained its primary ions.

Before bringing into contact with respective primary ions, the investigated ISEs (with one exception) exhibited almost Nernstian response to the discriminated ions. The exception was K$^+$ ISE, which did not show any response to Ca$^{2+}$. After being soaked in the solutions containing respective primary ions, all ISEs showed Nernstian behaviour and their response to the interferences was practically lost. The corresponding data are summarized in Table 2, and an example of this behavior is presented in Figure 3 for ISEs K1 and K2. All the measurements were performed in such a way that the internal and external electrolytes were the same and they differed only with respect to concentration. This is why the plots in Figure 3 lack large shifts between one another, which reflect the selectivity, and would appear if the internal solution is always the same.
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Table 2. Electrochemical parameters of the studied membranes **

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Aqueous electrolyte</th>
<th>S, mV</th>
<th>$R_p$, kOhm</th>
<th>$C_m$, pF</th>
</tr>
</thead>
<tbody>
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<td>KCl</td>
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<td>40</td>
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<tr>
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<td>NaCl$^{(b)}$</td>
<td>57.5</td>
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<td>35.7</td>
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<td>30</td>
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<td>KCl</td>
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<td>20</td>
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<td>20</td>
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<td>25.9</td>
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<td>KCl$^{(a)}$</td>
<td>31</td>
<td>23.2</td>
<td>70</td>
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<tr>
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<td>CaCl$_2$ (b)</td>
<td>37</td>
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<td>LiCl</td>
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<td>175</td>
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<td>LiCl</td>
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<td>47.0</td>
<td>1120</td>
<td>70</td>
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</table>

** S (the slope) values result from a linear treatment of the response within the range $10^{-1}$–$10^{-3}$ mol L$^{-1}$. Other values refer to 0.01 mol L$^{-1}$ of the respective electrolytes. Superscripts (b) and (a) refer to the data obtained before and after the first contact of the membrane with primary ions. The number of digits reflects the fitting error.
Figure 3. Potentiometric response of ISEs with K1 and K2 membranes in NaCl before contact with KCl (curves 1 and 2 respectively) and after such contact (curves 3 and 4).

In contrast to the potentiometric performance, the impedance spectra of ISEs were virtually the same in the solutions of the discriminated electrolyte (before and after soaking the electrodes in the solution containing primary ions), and also in the presence of respective primary ions (Fig. 4).

Figure 4. Impedance spectra of ISEs in electrolytes containing primary and discriminated ions (before and after contact with primary ions). A – ISE K1 in KCl (curve 1), in NaCl before contact with KCl (curve 2), and after contact with KCl (curve 3); B – ISE Na2 in NaCl (curve 1), in KCl before and after contact with NaCl (curves 2, 3), in CaCl2 before and after contact with NaCl (curves 4, 5); [32] (with permission from WILEY–VCH @ 2006); C – ISE Ca1 in CaCl2 (curve 1), in KCl before and after contact with CaCl2 (curves 2, 3), in NaCl before and after contact with CaCl2 (curves 4, 5); [32] (with permission from WILEY–VCH @ 2006); D – ISE Li1 in LiCl (curve 1), in NaCl (curve 2), and in KCl (curve 3); [30] (with permission from the American Chemical Society @ 2006). (Continuation on the next page)
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Figure 4. Continuation
The spectra exhibit a clear semicircle in the high frequency domain. In the low frequency domain of the spectra, the Warburg impedance (Z\textsubscript{W}) line was observed for most of the membranes. Therefore, the circuit shown in Figure 2C was used in the processing of the experimental data.

Among Na\textsuperscript{+}-selective membranes, potentiometric performance of Na\textsubscript{2} membrane undergoes the most drastic change after the first contact with NaCl. The impedance spectra obtained for this membrane are presented in Figure 4B. One can see that for K\textsuperscript{+} ions the spectra did not change significantly after the contact with Na\textsuperscript{+} ions. In CaCl\textsubscript{2}, both before and after the contact with NaCl, the membrane exhibited a finite Warburg diffusion behavior at low frequencies. Among Ca\textsuperscript{2+}-selective membranes, the biggest changes in the potentiometric performance were observed for Ca\textsubscript{1} membrane. However, the impedance spectra of the membrane recorded in the interfering electrolytes before and after the first contact with CaCl\textsubscript{2} do not differ significantly affected (Fig. 4C).

Lithium ISE (Li\textsubscript{1}) also gave only high-frequency semicircle in the impedance spectra, suggesting no kinetic hindrance for discriminated ions. However, the semicircle depended on the nature of the electrolyte, being the smallest for LiCl and the biggest for KCl (Tab. 2). In principal, bulk resistance must be constant except for the Donnan exclusion failure. It seems possible, however, that the discriminated ions in the membranes that are not complexed with neutral ionophore molecules are stronger bound to the ion exchanger sites, thus generating higher bulk resistance.

Electrochemical impedance spectra obtained for Li\textsubscript{2} ISE (without deliberately added sites) noticeably differed from those obtained for other membranes. Bulk semicircle in the high frequency domain was followed by another semicircle at lower frequencies. Because in the impedance spectrum two semicircles appeared, Li\textsubscript{2} membrane was treated by equivalent circuit B shown in Figure 2.

Two characteristic spectra (Fig. 5A) are shown to compare lithium membranes with and without ionic additive. After equilibration with 10\textsuperscript{−6} mol L\textsuperscript{−1} LiCl and applying 0.01 mol L\textsuperscript{−1} MgCl\textsubscript{2} as a background, the bulk resistance of Li\textsubscript{2} membrane without KCITPB was significantly higher than that of Li\textsubscript{1} membrane containing the same amount of a neutral ionophore and doped with the additive. It is even more interesting that the undoped membrane Li\textsubscript{2} also gave a huge low-frequency semicircle. It is known that plasticized PVC membranes contain anionic lipophilic impurities at concentrations up to 6 × 10\textsuperscript{−5} mol L\textsuperscript{−1} [35]. Most probably, these impurities are responsible for cationic response of Li\textsubscript{2} membrane.
Concentration dependence of the impedance spectra of ISE Li2 is presented in Figure 5B. The spectra were recorded in LiCl solutions with a constant background of 0.01 mol L$^{-1}$ MgCl$_2$. The constant background was applied to avoid possible problems with silver/silver chloride electrodes at low concentration of chloride and to prevent the unwanted effect of solution resistance. MgCl$_2$ was chosen since Mg$^{2+}$ ions affect the Li$^+$ response only slightly (even 0.1 mol L$^{-1}$ Mg$^{2+}$ does not interfere with 10$^{-5}$ mol L$^{-1}$ LiCl) and intuitively seems to be the most appropriate inert supporting electrolyte for kinetic measurements.

The obtained results are presented in Figure 5B. Li2 membrane without ionic additive gave a low-frequency semicircle regularly dependent on LiCl concentration. This regularity suggests the Faradaic nature of the semicircle. In particular, the log($R_2$)
vs logC_{Li} plots were linear and allowed one to estimate charge transfer coefficient for Li\(^+\), which equaled 0.6. This value being close to the theoretically expected 0.5 gave an additional evidence of a Faradaic origin of the low-frequency semicircle.

CONCLUSIONS

Electrochemical equilibrium at the interface between an ISE membrane and aqueous solutions, normally, is taken for granted. This idea is backed by Nernstian or nearly Nernstian response of ISEs to the primary ions. It is known that the response to the discriminated ions is sub-Nernstian, or becomes sub-Nernstian once the membrane is immersed into a solution containing primary ions. The lack of full slope in case of discriminated ions is attributed solely to the contamination of solutions with primary ions from membranes. The alternative explanation, not sufficiently explored yet, is that interfacial charge transfer of discriminated ions is inhibited once ionophore is „occupied” with primary ions.

Potentiometric and impedance studies of ISE membranes were carried out, and the results were carefully interpreted to provide data favoring the traditional concept (contamination). Thus, no breakthrough in our knowledge on ISEs was achieved. However, this commonly adopted concept, due to the obtained data, has got more solid base.

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REFERENCES

AC-impedance studies of ion transfer across ionophore-based ion-selective membranes