analytical chemistry

Letter

pubs.acs.org/ac

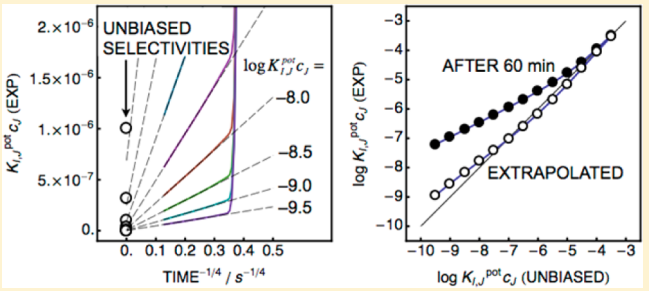
Evaluation of Egorov's Improved Separate Solution Method for Determination of Low Selectivity Coefficients by Numerical Simulation

Eric Bakker*

Department of Inorganic and Analytical Chemistry, University of Geneva, Quai E.-Ansermet 30, 1211 Geneva, Switzerland

Supporting Information

ABSTRACT: The group of Egorov has recently proposed an elegant method to determine unbiased selectivity coefficients of ion-selective electrodes (Egorov et al. *Anal. Chem.* **2014**, *86*, 3693). Once the electrode is exposed to a solution containing only interfering ions, the time-dependent experimental selectivity coefficients are plotted as a function of the inverse fourth root of time and extrapolated to zero. The principal assumption of the approach is the progression of the diffusion layer in the membrane phase with square root of time. This letter critically evaluates the usefulness of this methodology by finite element analysis. The results suggest that the improvement of observed selectivity values are highly significant for an initially uniform distribution of primary ions across the membrane, strongly supporting the methodology. When strong inward ion fluxes of primary ions are present instead, a modification of the method by extrapolation of logarithmic selectivity coefficients appears to give the best results.



The selectivity coefficients measured for membrane electrodes of high selectivity are often biased when the membranes are conditioned with a solution of the preferred primary ion. This is because this ion must be quantitatively exchanged by the interfering ion within the diffusion layer of the membrane to obtain a potential that depends only on the interfering ion in a nernstian manner.[1] A range of methods has been proposed to overcome this limitation, including conditioning the membrane with a less preferred ion[1] and imposing strong inward fluxes by adding a complexing agent in the inner solution during measurement of the interfering ion.[2]

When a membrane is exposed to a solution containing interfering ion salt, the primary ion activity at the membrane surface (position 0) is approximated by counterdiffusion processes as follows (see Supporting Information for full details):[3]

$$a_I^{aq}(0) = (K_{I,J}^{pot} a_J^{aq} q c_I^{m*})^{1/2} \quad (1)$$

where $K_{I,J}^{pot}$ is the selectivity coefficient, a_J^{aq} is the interfering ion activity, c_I^{m*} is the primary ion concentration in the bulk of the membrane, and q is the permeability ratio, defined as

$$q = \frac{D_I^m \delta_I^{aq}}{D_I^{aq} \delta_I^m(t)} \quad (2)$$

where D indicate the diffusion coefficients for I and δ the diffusion layer thickness in the indicated phase. If one assumes that $\delta_I^m(t)$ increases with time according to $\delta_I^m(t) = (\pi D_I^m t)^{1/2}$, this relationship is inserted into eq 2 and then combined with eq 1 to obtain[4]

$$a_I^{aq}(0) = \left(K_{I,J}^{pot} a_J^{aq} \frac{\sqrt{D_I^m} \delta_I^{aq}}{\sqrt{\pi} D_I^{aq}} c_I^{m*} \right)^{1/2} t^{-1/4} \quad (3)$$

Extrapolating experimental selectivity coefficients plotted against $t^{-1/4}$ to a value of $t^{-1/4} = 0$ ($t \rightarrow \infty$) should approach the situation where $a_I^{aq}(0) = 0$, thereby eliminating the experimental selectivity bias.[4]

RESULTS AND DISCUSSION

We simulate experimental behavior by finite difference analysis, based broadly on the approach described by Morf (see the Supporting Information for details).[5] In a first set of calculations, the concentration of primary ion at the inner side is assumed to be equal to the ion-exchanger concentration. This case is known to exhibit the lowest operational detection limit of the ion-selective electrode since it minimizes zero current counter- and codiffusion fluxes of primary ion across the membrane.[3,6] Figure 1 shows the apparent selectivity coefficients as a function of time upon exposure to interfering ion solution for the indicated unbiased selectivity values. It is apparent from the diminishing vertical distance of the curves that the observed selectvity coefficients start being biased for log$K_{I,J}^{pot} c_J$ values smaller than −4.5.

Egorov's extrapolation approach is demonstrated with the same data set in Figure 2, where the values are replotted as a

Received: July 17, 2014
Accepted: August 6, 2014
Published: August 6, 2014

   dx.doi.org/10.1021/ac502638s | *Anal. Chem.* 2014, 86, 8021−8024

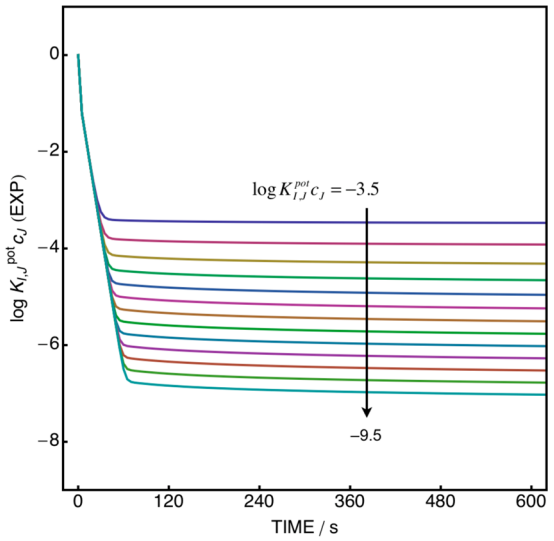


Figure 1. At time zero, the sample solution is changed to one containing interfering ions only, and the potential is monitored over time, displayed here to show the apparent selectivity coefficient. The curves correspond to different unbiased selectivities in steps of 0.5 orders of magnitude with a membrane containing a primary ion concentration equal to the ion-exchanger concentration (balanced membrane).

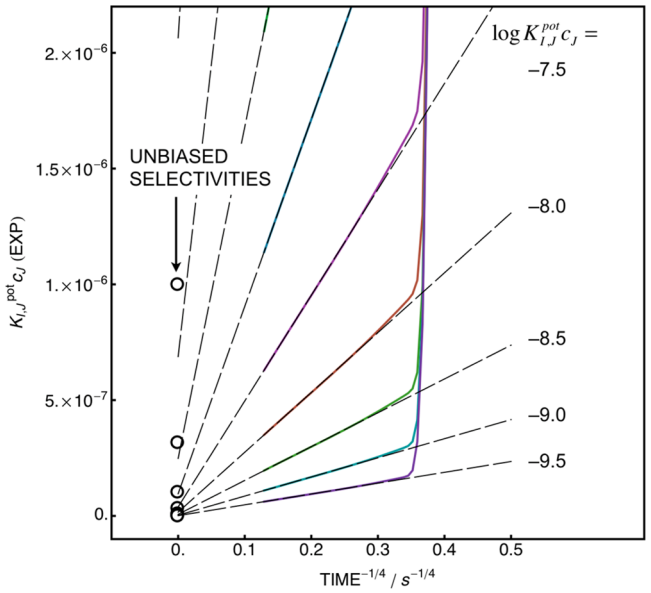


Figure 2. Egorov's extrapolation approach dashed lines according to eq 3, shown for the data in Figure 1. Open circles mark the unbiased selectivity coefficients for the series.

function of the inverse fourth root of time. The values extrapolated to zero appear to be generally quite close to the unbiased selectivity values shown as open circles. In this graph, the correlation is difficult to discern for values better than about log $K_{I,J}^{pot} = -7.5$, but we will see that it is still adequate for very large selectivities.

Egorov's methodology assumes that the membrane diffusion layer follows the behavior $\delta_I^m(t) = (\pi D_I^m t)^{1/2}$. The simulated time-dependent membrane concentration profiles for the case of best selectivity is shown in Figure 3 (10 min time interval shown). From this data set, the diffusion layer thickness was calculated by linear extrapolation of the interfacial membrane

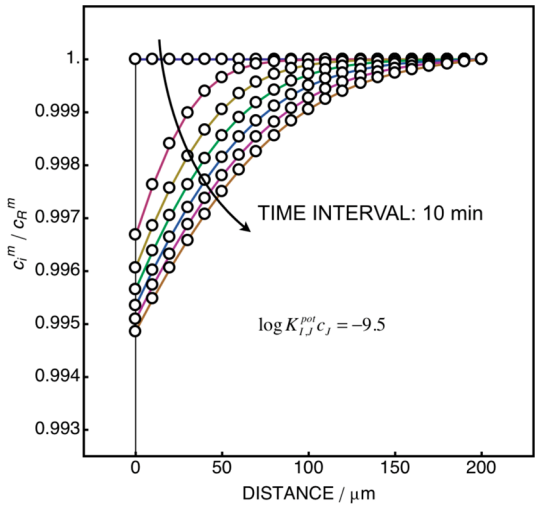


Figure 3. Time-dependent membrane concentration profiles (10 min interval shown) relative to the ion-exchange concentration, c_R^m, for the indicated selectivity and with the data from Figure 1

concentration gradient (element 0 and 1 in the simulation) to the bulk membrane concentration. This distance was plotted as a function of the square root of time, confirming linear behavior (see Figure 4). All other selectivities gave linear behavior as well (not shown).

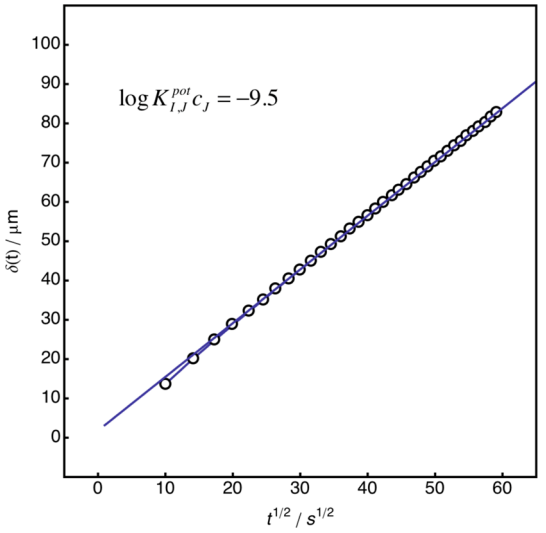


Figure 4. Confirmation of the key assumption of the approach, $\delta_I^m(t) = (\pi D_I^m t)^{1/2}$ using the simulated membrane concentration data for the case of best selectivity.

Nonetheless, it was found that the extrapolation approach fails for extremely large selectivies if the potentials are not sampled for sufficiently long times (see Figure 5). While a 10 min sampling time appears to be sufficient for log $K_{I,J}^{pot} c_J = -7.0$, longer experimental times of up to 60 min are required for systems of excellent selectivity. Otherwise, one may obtain physically implausible negative selectivity coefficients. In these more extreme cases, the extrapolated selectivity is more than 2 orders of magnitude smaller than the value suggested from the last potential reading, see Figure 2.

Figure 6 compares the experimental selectivity coefficients obtained by Egorov's approach with the values obtained from

dx.doi.org/10.1021/ac502638s | Anal. Chem. 2014, 86, 8021−8024

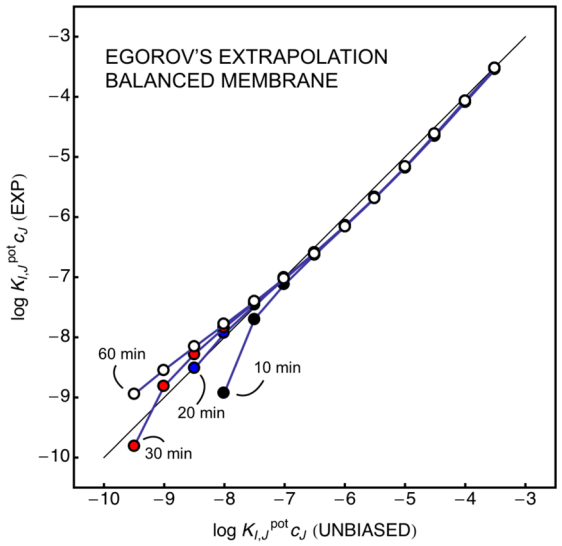


Figure 5. Experimental selectivity coefficients for the data shown in Figure 1 obtained from Egorov's approach (Figure 2) and comparison to ideal behavior (no bias). Increasing experimental times reduces the uncertainty of the method.

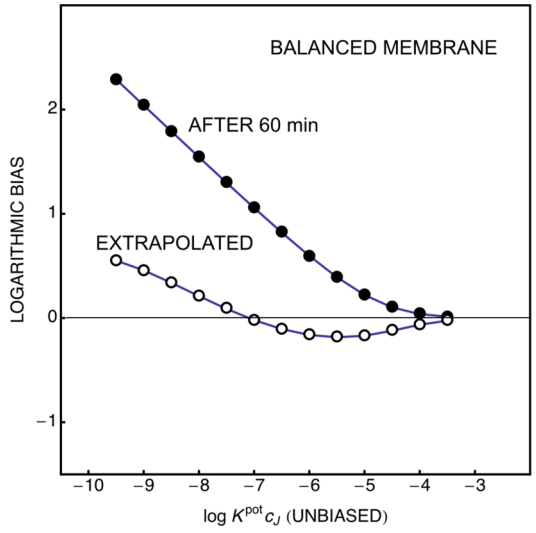


Figure 6. Experimental selectivity coefficients for the data shown in Figure 1 using simple potential readings and Egorov's approach (Figure 2), and comparison to ideal behavior (no bias).

traditional potential readings after 60 min of exposure time. With the new method, the bias is generally acceptable, at most half an order of magnitude, while the traditional method fares significantly worse.

Two more cases were considered in this study. If one assumes a strong outward flux of primary ions from the membrane by cotransport from the inner solution (see Supporting Information for details), the results are initially comparable to those discussed above, but at high selectivities of log $K_{I,J}^{pot} < -5.0$, the membrane potential becomes dictated by the outflux of primary ion salt and the methodology starts to fail (Figure 7).

We now consider a case with a strong inward ion flux owing to quantitative displacement of primary ion by interfering ones at the inner solution side of the membrane. Such compositions have earlier been suggested to be very useful for the

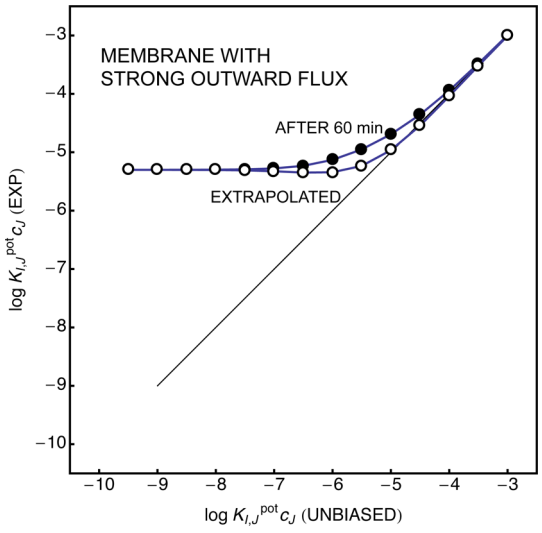


Figure 7. Experimental selectivity coefficients for the data shown in Figure 1 using simple potential readings and Egorov's approach (Figure 2) and comparison to ideal behavior (no bias).

determination of unbiased selectivity coefficients,[2] but a rigorous treatment has not yet been put forward.

As shown in Figure S6 in the Supporting Information, Egorov's extrapolation procedure fails to give chemically meaningful values for membranes of good selectivity, as the simulated data for log $K_{I,J}^{pot} c_J = -7.0$ are clearly nonlinear. This is likely due to the strong inward gradient of the primary ion within the membrane, which makes it difficult to fulfill the assumptions required in the approach.

Surprisingly, an adaptation of the methodology gives excellent results for situations exhibiting a strong inward flux. If the time-dependent *logarithmic* experimental selectivity coefficient is plotted on the *y*-axis, extrapolation to the unbiased values is successful for all selectivities studied in the simulation (see Figure S7 in the Supporting Information). This modified approach appears to give much better selectivity values than traditional potential readings. The reason for this is not immediately clear. Figure S8 in the Supporting Information shows the simulated concentration profiles for the case of highest selectivity studied here to show how the membrane concentrations evolve over time. Figure 8 compares this modified method with traditional readings, suggesting the significant reduction of any bias even with membranes of strong inward ion fluxes.

In conclusion, Egorov's methodology is elegant and useful and should be clearly adopted by researchers in the field. The results appear to be quite spectacular for so-called balanced membranes where transmembrane ion fluxes are kept to a minimum. For membranes exhibiting strong inward fluxes it appears more appropriate to extrapolate *logarithmic* selectivity coefficients, but the reasons for this are not yet understood. In all cases, the reliability of the method should be confirmed with different interfering ion concentrations giving the same selectivity value, as originally proposed by Egorov and co-workers.[4]

dx.doi.org/10.1021/ac502638s | *Anal. Chem.* 2014, 86, 8021−8024

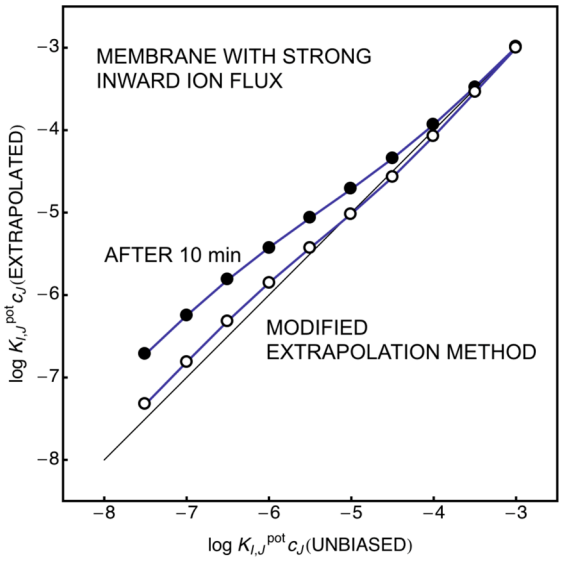


Figure 8. Simulated logarithmic selectivity coefficients for membranes exhiting a strong inward ion flux, using the modified method of extrapolating *logarithmic* selectivity coefficients (open circles) and the potentials after 10 min experimental time (black circles).

■ ASSOCIATED CONTENT

Supporting Information

Derivation of Egorov's approach, details of simulations, and additional data. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: eric.bakker@unige.ch.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the Swiss National Science Foundation.

■ REFERENCES

(1) Bakker, E. *Anal. Chem.* **1997**, *69*, 1061−1069.
(2) Sokalski, T.; Ceresa, A.; Zwickl, T.; Pretsch, E. *J. Am. Chem. Soc.* **1997**, *119*, 11347−11348.
(3) Ceresa, A.; Bakker, E.; Hattendorf, B.; Gunther, D.; Pretsch, E. *Anal. Chem.* **2001**, *73*, 343−351.
(4) Egorov, V. V.; Zdrachek, E. A.; Nazarov, V. A. *Anal. Chem.* **2014**, *86*, 3693−3696.
(5) Morf, W. E.; Pretsch, E.; De Rooij, N. F. *J. Electroanal. Chem.* **2007**, *602*, 43−54.
(6) Peper, S.; Ceresa, A.; Bakker, E.; Pretsch, E. *Anal. Chem.* **2001**, *73*, 3768−3775.