TOWARDS SINGLE-ION SENSITIVE IONOPHORE-BASED OPTODES: THEORETICAL SOLUTION AND EXPERIMENTAL VALIDATION

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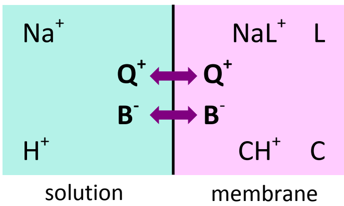
INTRODUCTION

Ion-selective optical sensors are rapidly developing instruments in biological research. They can be miniaturized down to nano-size devices thus providing minimally and even non-invasive measurements attractive for *in vivo* use. Nano-size optodes have been approved for a first-in-human clinical trial [1]. However, bulk optodes can only detect either a ratio or a product of the two ion activities — of the analyte and of the reference ion [2]. Typically, pH or ionic strength of the sample must be known *a priori* or independently determined. We propose here a fundamental approach for developing an optode sensitive to the individual ion activity (pH in this study).

THEORY

Ion-exchange equilibrium:

$$CH^+_{(m)} + Na^+_{(aq)} + L_{(m)} + Q^+_{(m)} + B^-_{(m)} \overset{K_{exch}}{\Longleftrightarrow} C_{(m)} + H^+_{(aq)} + NaL^+_{(m)} + Q^+_{(aq)} + B^-_{(aq)}$$



QB — electrolyte of moderate lipophilicity [3]

Signal: $\alpha = \dfrac{[C]}{[C]+[CH^+]}$

$$\underbrace{\ln\left(\frac{1-\alpha}{\alpha}\right)}_{\text{signal}} = \underbrace{\ln a_H}_{\text{analyte}} - \underbrace{\ln\frac{K_a}{k_H} - 2\ln\frac{k_l}{k_Q k_B}}_{\text{constant}} + \underbrace{\frac{F}{RT}(\varphi^m - \varphi^{aq})}_{\text{stabilized}}$$

Galvani-potential is governed by the partitioning of QB

$$\alpha = f(a_H) \text{ and } \alpha \neq f(a_{Na})$$

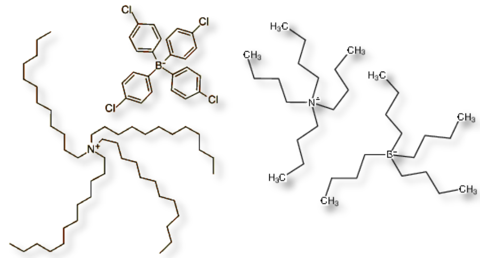
MATERIALS AND METHODS

PVC, Na$^+$ ionophore VI, chromoionophore, DOS

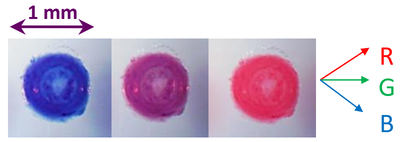
+

QB: stabilizes the Galvani-potential

ETH500 **TBATBB**



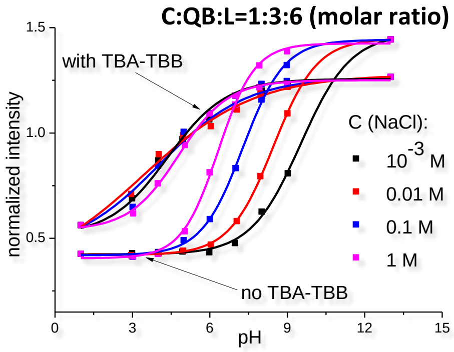
Signal acquisition: microphotography + digital color analysis



pH 6 pH 7.5 pH 9

RESULTS AND CONCLUSIONS

C = ETH5350 L = NaVI QB = TBATBB

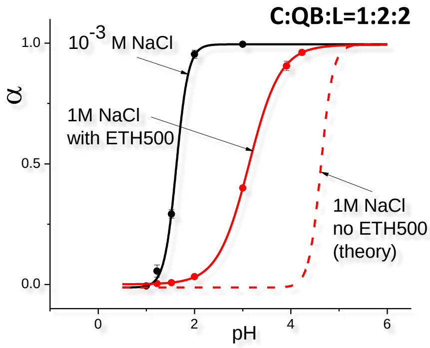


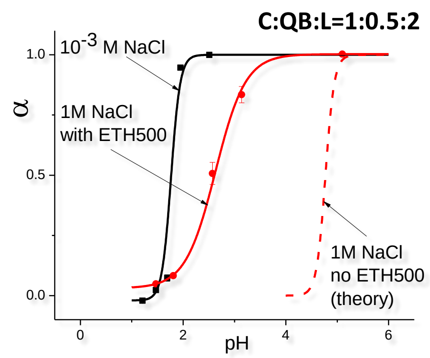
NO effect of ionic strength!

BUT:

- outside physiological range
- effect of components nature?
- effect of components content?

C = ETH2439 L = NaVI QB = ETH500





shift of the dynamic range with 3-orders change of the ionic strength (in log units)

composition	ETH500	TBA-TBB
no QB (conventional)	3	3
C:QB:L=1:0.5:2	1.5	1.3
C:QB:L=1:1:2	0.8	0.8
C:QB:L=1:2:2	0.8	no function
C:QB:L=1:2:4	?	?
...	?	?
C:QB:L=1:3:6	?	0

ACKNOWLEDGEMENTS AND REFERENCES

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[1] M. Benezraet et al., J. Clin. Invest., 2011, 121, 2768 [2] E. Bakker et al., Chem. Rev., 1997, 97, 3083 [3] S. Anastasova-Ivanova et al., Sens. Actuators B, 2010, 146, 199.