

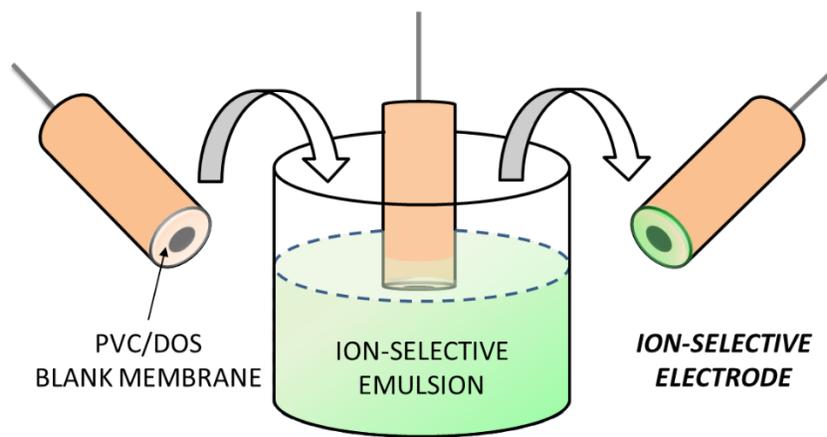
Supporting information for:

## Emulsion Doping of Ionophores and Ion-Exchangers into Ion-Selective Electrode Membranes

Yoshiki Soda<sup>a</sup>, Wenyue Gao<sup>a</sup>, Jérôme Bosset<sup>b</sup> and Eric Bakker<sup>a\*</sup>

<sup>a</sup> Department of Inorganic and Analytical Chemistry, University of Geneva, Quai Ernest-Ansermet 30, CH-1211 Geneva, Switzerland.

<sup>b</sup> BioImaging Center, Department of Biochemistry, University of Geneva, Quai Ernest-Ansermet 30, CH-1211 Geneva, Switzerland.



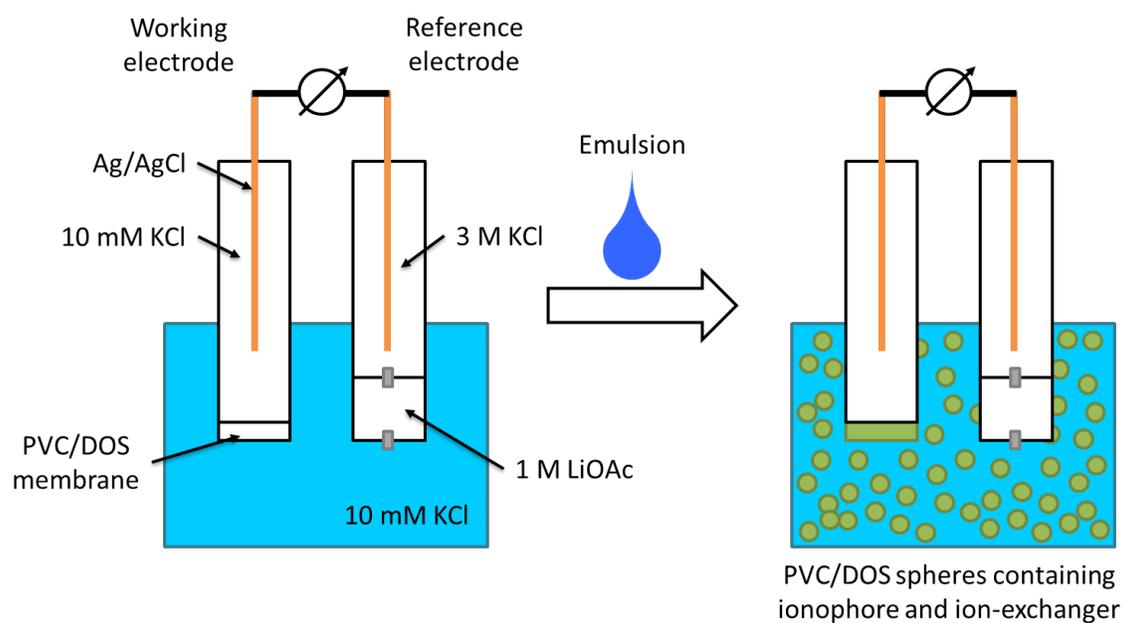


Figure S1. Schematic illustration of the experimental mass transfer of ionophore and ion-exchanger from emulsified plasticized PVC to an originally pristine membrane free of sensing components to endow it with  $K^+$  selectivity.

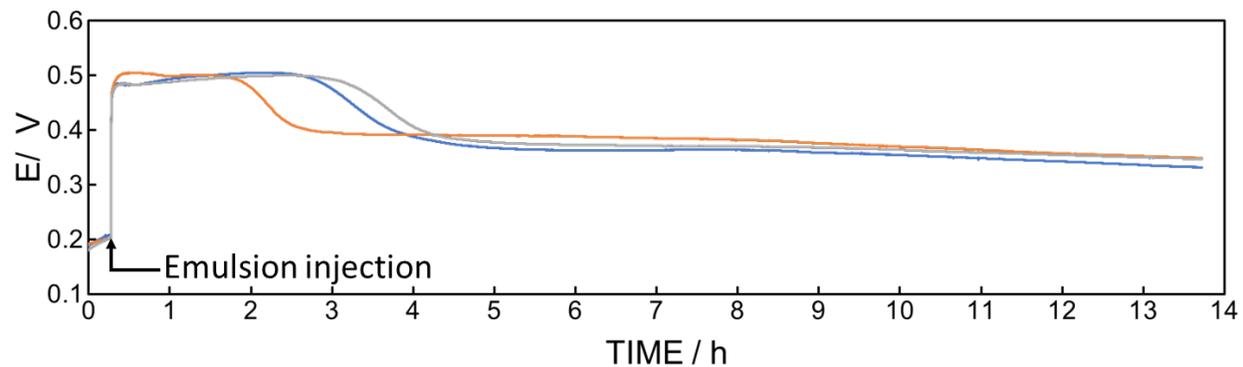


Figure S2. Recorded potential-time trace during emulsion doping with valinomycin and KTFPB for three all-solid-state electrodes with blank plasticized PVC (PVC:DOS = 1:2) and a conductive POT transducing layer. The abrupt potential increase marks the time when the polymeric emulsion composed of PVC/DOS (1:2), valinomycin and KTFPB is added to the KCl solution, resulting in extraction of sensing components into the membrane. The partial potential reversal after 2 to 4 h suggests that the inner membrane potential is influenced by the diffusing sensing components.

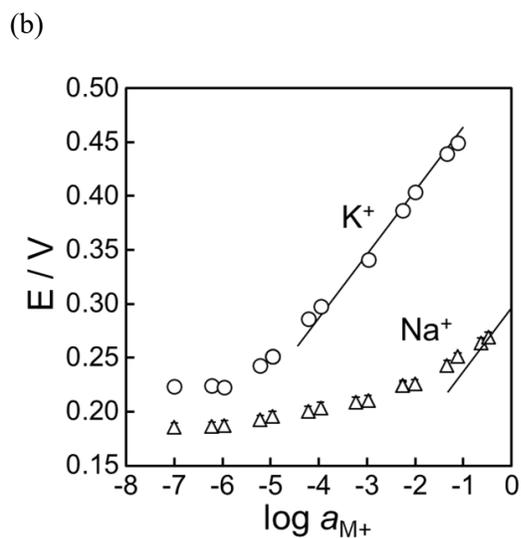
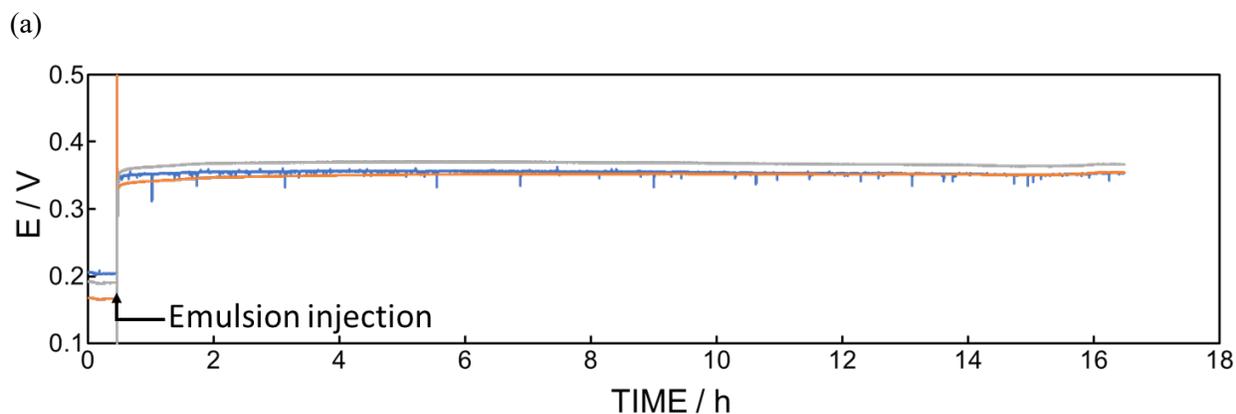


Figure S3. (a) Potential-time trace during emulsion doping for three all-solid-state electrodes as in Figure S1, but fabricated with less diffusive PVC membranes (PVC:DOS = 3:1). (b) Corresponding potentiometric response to  $K^+$  and  $Na^+$  after doping is complete. The solid lines with Nernstian slopes. See Table 1 for the experimental slope values.

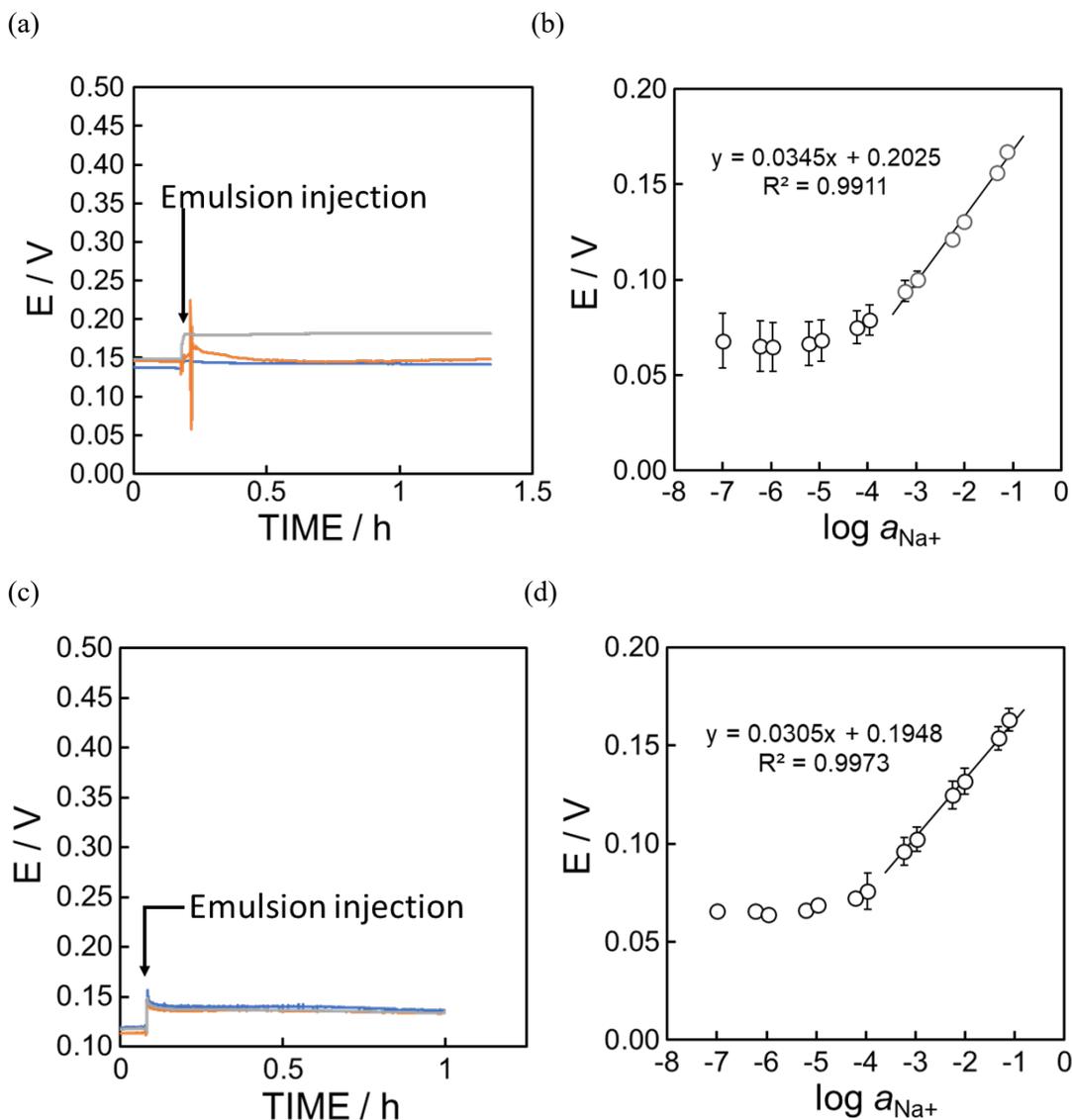


Figure S4. (a) Observed potential-time traces during the attempted doping of Na-X and NaTFPB from PVC/DOS (1:2) emulsion into three polymeric membranes (PVC:DOS = 1:2). (b) Subsequent lack of Nernstian response to Na<sup>+</sup>. (c) Doping as in a) but from Pluronic® F-127 with (d) the corresponding potentiometric response to Na<sup>+</sup>. See also Table 1 for the slope values.

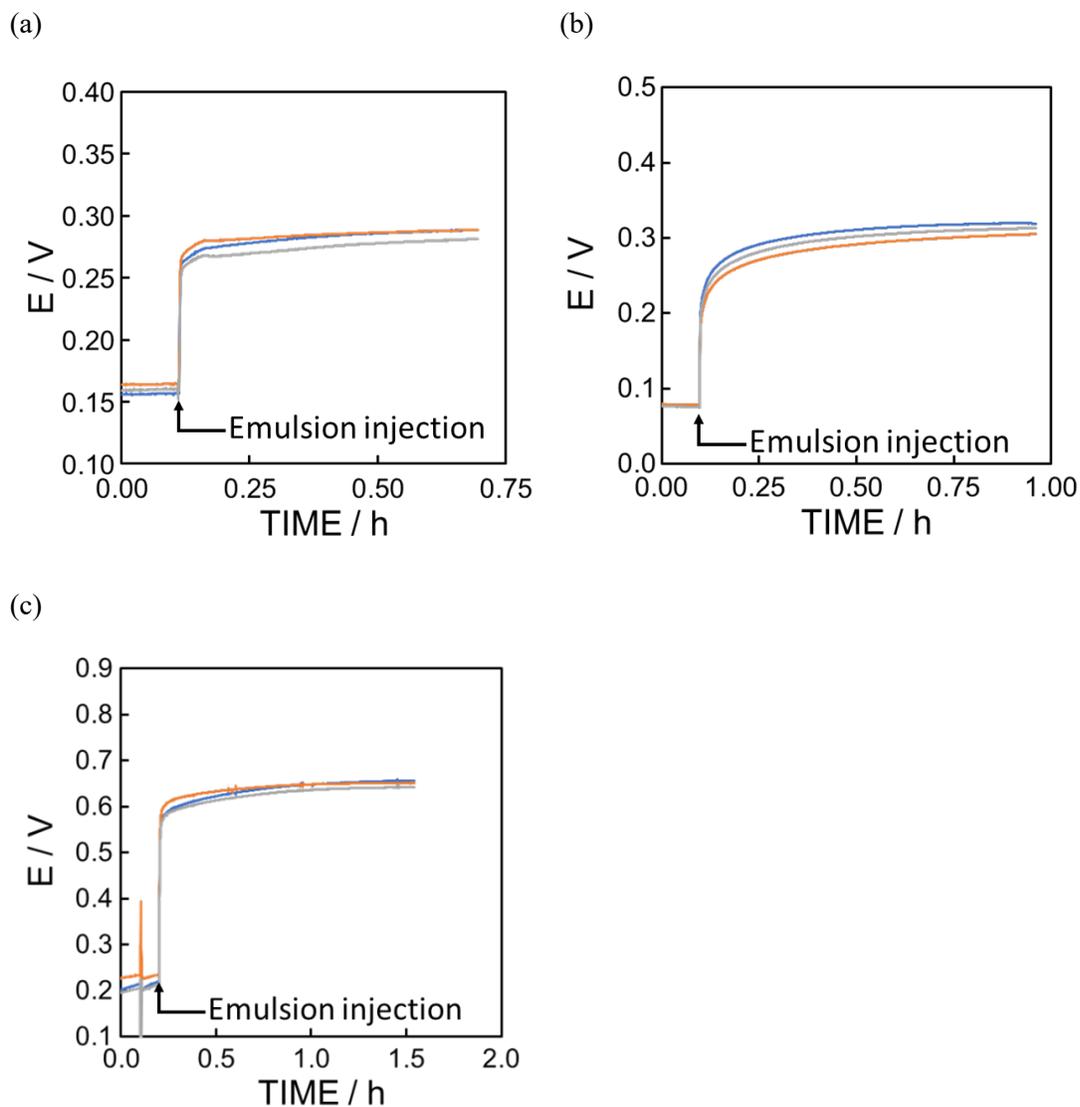


Figure S5. Potential transients of solid state electrodes with PVC/DOS containing a POT transducing layer upon addition of a DMF-based matrix-free emulsion containing (a) Na-X and NaTFPB for sodium (b) Ca-II/KTFPB for calcium and (c) TDMANO<sub>3</sub> for nitrate into solutions containing the appropriate analyte ion salt (see main text).

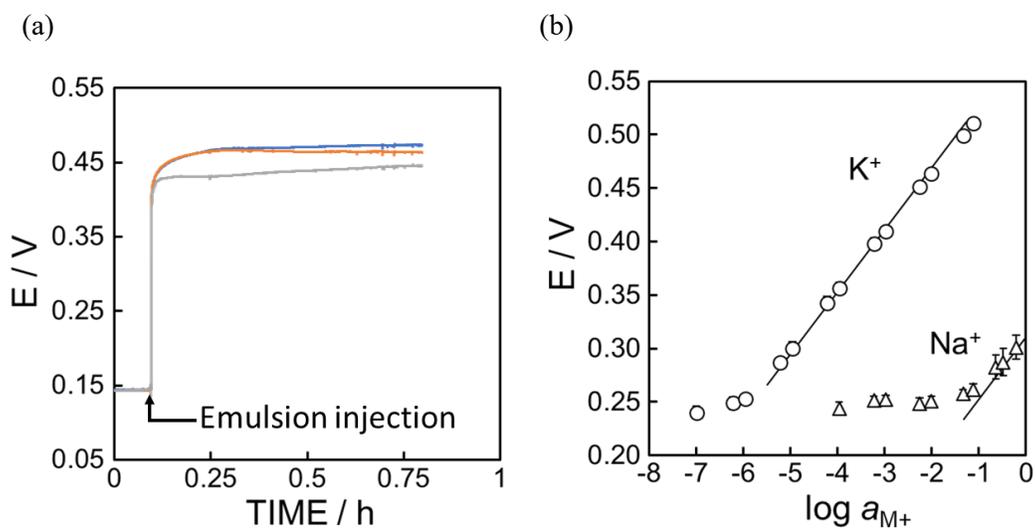


Figure S6. (a) Potential transients for three all-solid-state electrodes containing a blank plasticized PVC membrane (PVC:DOS = 1:2) doping with DMF-based matrix-free emulsions system containing valinomycin and KTFPB. (b) Corresponding potentiometric responses to  $K^+$  and  $Na^+$ . Solid lines are Nernstian (see Table 1 for experimental slopes).

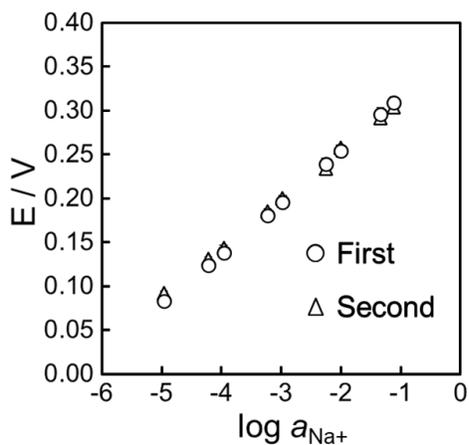


Figure S7. Repeated potentiometric calibration curves to  $Na^+$  by electrodes prepared by doping with a Na-X/NaTFPB-based DMF emulsion.



Figure S8. Picture of chromoionophore I fluorescence signal in the PVC/DOS membrane (1:2 mass ratio) observed by confocal microscopy. Conditions otherwise as for Figure 1b.

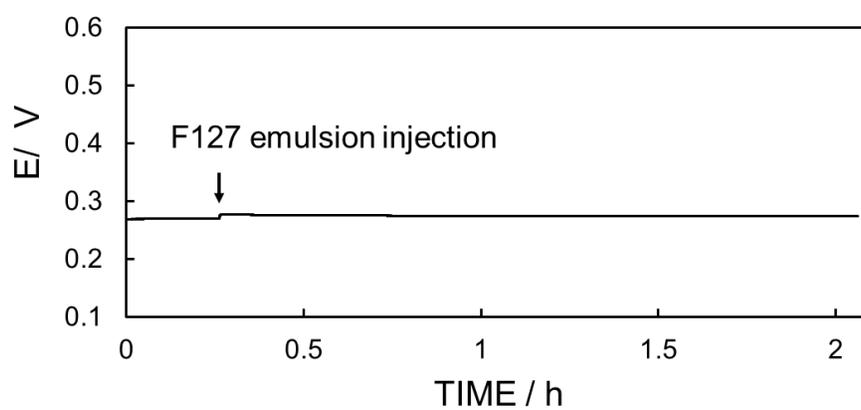


Figure S9. Prolonged exposure of a membrane containing  $10 \text{ mmol kg}^{-1}$  of valinomycin and  $3.3 \text{ mmol kg}^{-1}$  of KTFPB to an F-127/DOS emulsion, showing negligible potential drift.