

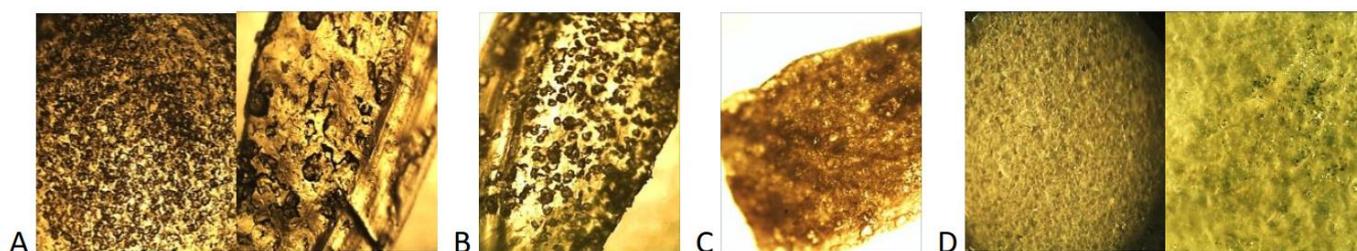
Supplementary material

## Response Mechanism of Polymeric Liquid Junction-Free Reference Electrodes Based on Organic Electrolytes

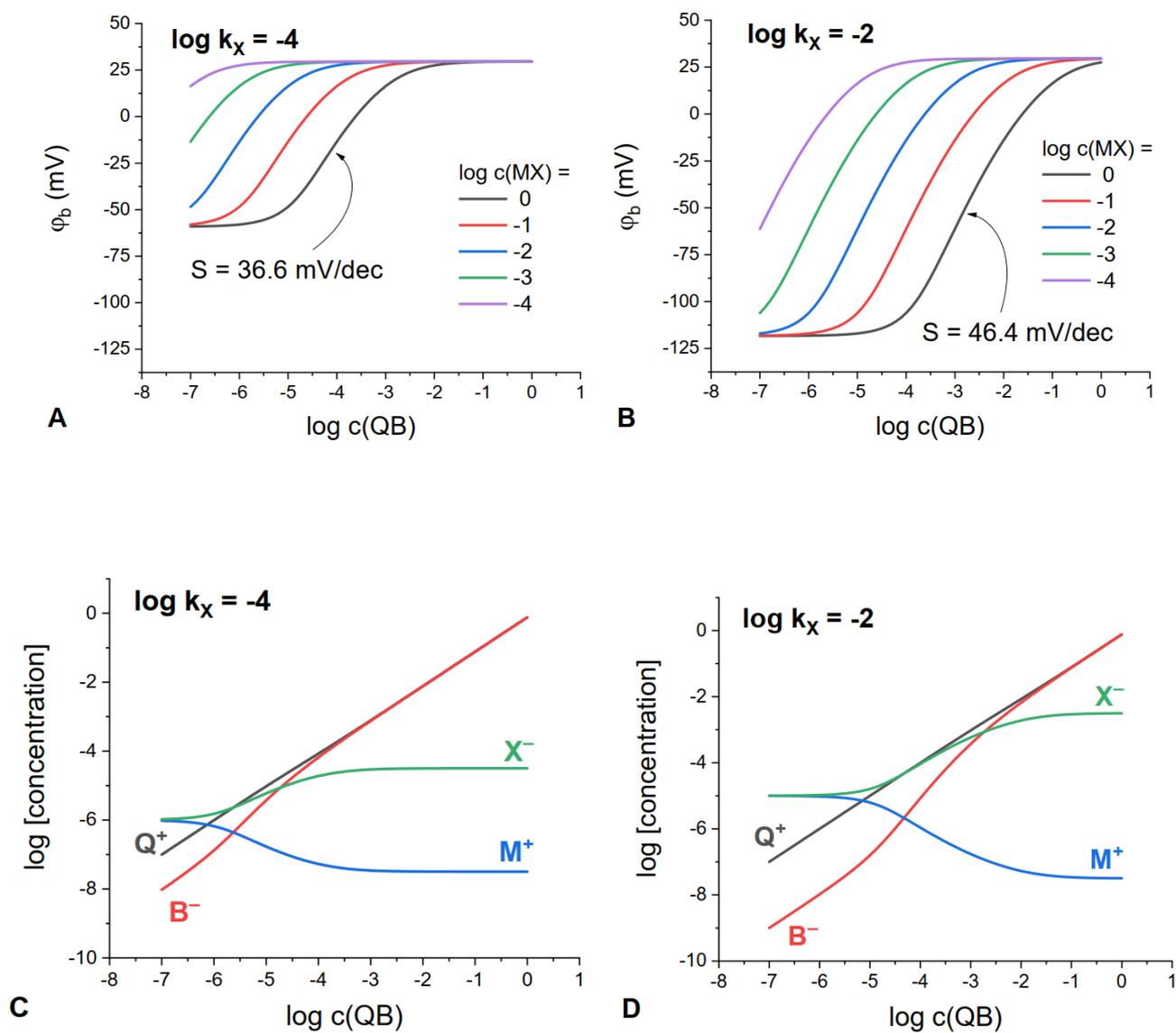
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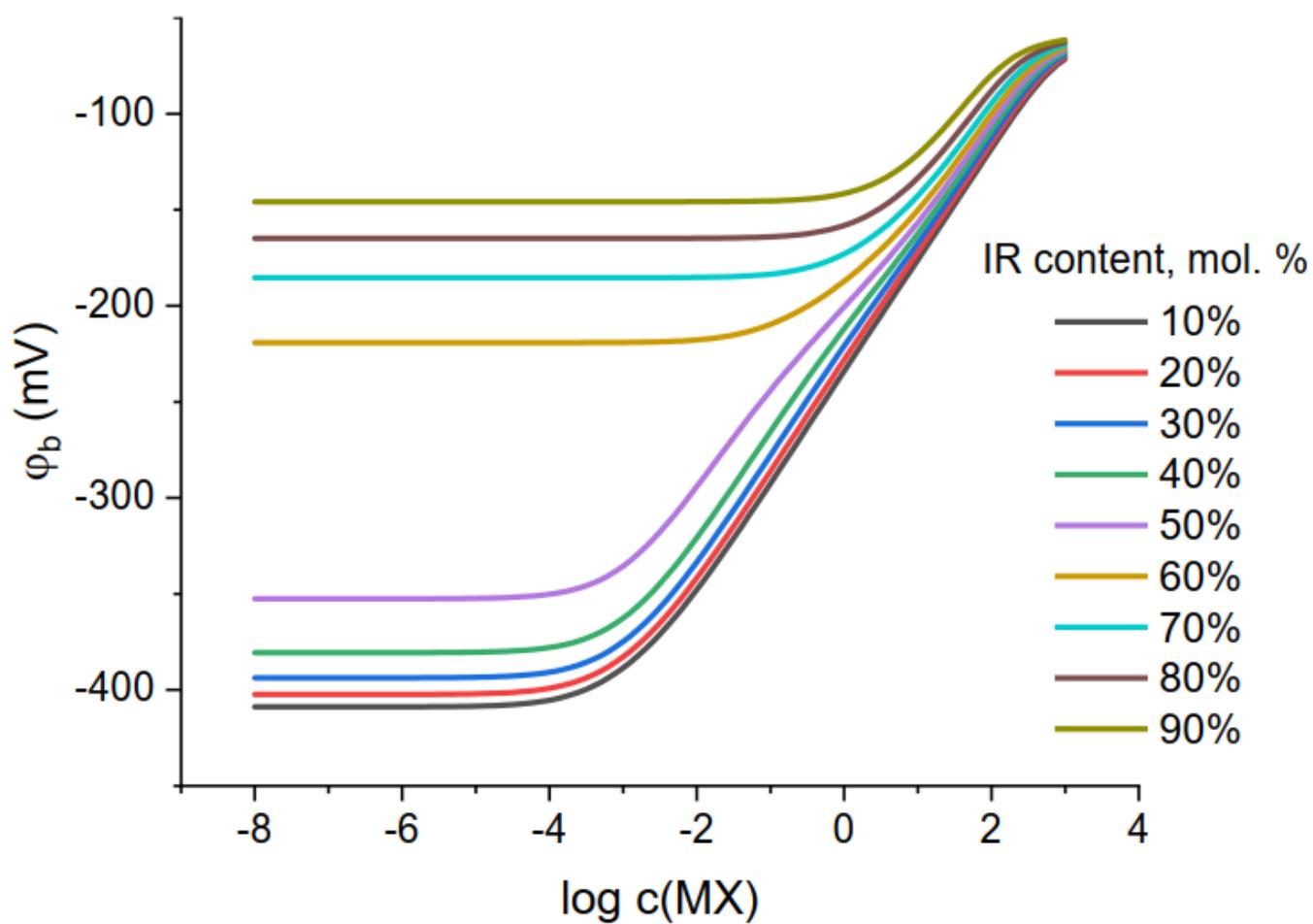
**Figure S1.** Freshly prepared (A); 5 min (B); 1 day (C) and 1 week (D) conditioned membranes containing TBATBB and dry KCl. Conditioning solution: 0.01 M KCl.



**Figure S2.** (A, B) Calculated dependences of the phase boundary potential on the Q<sup>+</sup>B<sup>-</sup> content in the polymeric phase at varied MX concentration in the aqueous phase (indicated in the plot) for two different partition coefficients of the aqueous anion X<sup>-</sup>. (C, D) The respective concentration profiles in the polymeric phase at  $c(MX) = 0.1$  M. Ionic partition coefficient of X<sup>-</sup> is indicated in the plot.  $k_M = 10^{-6}$ ;  $k_Q = 10^3$ ,  $k_B = 10^2$ .

**Table S1.** The characteristics of the response of the electrodes containing both KTpCIPB and ETH500 in the membrane.

	KCl	NH <sub>4</sub> Cl	CsCl	NaCl
mean slope for Nernstian response (below equimolar Q <sup>+</sup> B <sup>-</sup> to IR ratio), mV/dec	57.5 ± 0.5	57.5 ± 0.6	57.4 ± 0.4	59.0 ± 0.5
mean slope (above equimolar Q <sup>+</sup> B <sup>-</sup> to IR ratio), mV/dec	2.5 ± 1.3	5.2 ± 1.4	0.8 ± 1.8	3.8 ± 0.8
mean E value, mV	99.4 ± 5.2	140.1 ± 8.8 mV	125.0 ± 4.8	155.7 ± 6.2



**Figure S3.** The simulated response curves for the membranes containing both IR and Q+B in molar ratios from 10 to 90% (indicated in the plot).  $k_M = 10^{-6}$ ,  $k_X = 10^{-4}$ ,  $k_Q = 10^9$ ,  $k_B = 10^5$ ;  $k_I = 10^{-5}$ ;  $c(QB + IR) = 10^{-2}$  M.