Electronic Supplementary Material (ESI) for ChemComm.

Supporting information for

Ionophore-Based Ion-Exchange Emulsions as Novel Class of Complexometric Titration Reagents

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Experimental Section

Reagents:

Pluronic F-127 (F127), bis(2-ethylhexyl)sebacate (DOS), 2-nitrophenyl octyl ether (o-NPOE), dodecyl 2-nitrophenyl ether (D-NPOE), tetradodecylammonium tetrakis(4-chlorophenyl)borate (ETH 500), tetrahydrofuran (THF), sodium tetrakis-[3,5-bis(trifluoromethyl)phenyl]borate (NaTFPB), potassium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (KTFPB), calcium ionophore II (ETH 129), calcium ionophore IV, lead ionophore IV, poly(vinyl chloride) (PVC), $CaCl_2$, $Pb(NO_3)_2$, ethylenediaminetetraacetic acid disodium salt dehydrate (Na_2EDTA), 2-amino-2-hydroxymethyl-propane-1,3-diol (Tris) , hydrochloric acid (HCl) and Eriochrome Black T (EBT) were obtained from Sigma-Aldrich. Super pure nitric acid (65% w/w) was obtained from MERCK. Methyl methacrylate-decyl methacrylate copolymer (MMA-DMA) was synthetized in our group[1]. Arve River sample was obtained from Geneva, Switzerland.

Preparation of Ca^{2+}-selective and Pb^{2+}-selective emulsion:

For Ca^{2+}-selective emulsion, 2.24 mg of calcium ionophore II, 1.24 mg of KTFPB, 8.0 mg of D-NPOE and 3.0 mg of F127 were dissolved in 2.0 mL of THF to form a homogeneous solution. 0.5 mL of this THF solution was pipetted and injected into 3 mL of deionized water vortexing at 1000 rpm. Compressed air was blown on the surface for 30 min to remove THF.

For Pb^{2+}-selective emulsion, 1.83 mg of lead ionophore IV, 0.63 mg of KTFPB, 6.08 mg of D-NPOE, and 2.48 mg of F127 were dissolved in 2.0 mL of THF, followed by the procedure above.

Membranes and electrodes:

The Ca^{2+}-selective membrane was prepared by dissolving the mixture composed of 16.5 mmol/kg of calcium ionophore IV, 6.9 mmol/kg NaTFPB, 63.1 wt% o-NPOE, and 33.5 wt% PVC in 1.5 mL THF. For Pb^{2+}-selective membranes, the membranes optimized for low detection limits contained 0.74 mmol/ kg lead ionophore IV, 0.34 mmol/kg NaTFPB, 10.98 mmol/kg ETH 500, 33.00 wt% MMA-DMA, 22.80 wt% DOS, 42.83 wt% PVC, and 0.17 mmol/kg $Pb(NO_3)_2$. The cocktail solution was then poured into a glass ring (22 mm in diameter) placed on a glass slide and dried overnight at room temperature under a dust-free environment. Small disks were punched from the cast films and conditioned for 2 days in 5×10^{-9} M $Pb(NO_3)_2$ (diluted by 10^{-4} M HNO_3) for Pb^{2+}-selective membranes, and corresponding Ca^{2+}-selective membranes in 5×10^{-9} M $CaCl_2$. The conditioned membranes were mounted separately in Ostec electrode bodies (Ostec, Sargans, Switzerland). For the Ca^{2+} ISE, 10^{-2} M Na_2EDTA, 10^{-4} M $CaCl_2$, adjusted to pH 7.0 with NaOH, was used as inner filling solution. For the Pb^{2+} ISE with a low detection limit, 10^{-2} M Na_2EDTA, 10^{-4} M $Pb(NO_3)_2$, adjusted to pH 7.0 with NaOH, was used as inner filling solution.

Instrumentations and measurements:

Potentiometric titration signals were recorded on an EMF-16 precision electrochemistry EMF interface from Lawson Laboratories, Inc. A double-junction Ag/AgCl was used as reference electrode (Mettler-Toledo AG, Schwerzenbach, Switzerland).

For potentiometric calcium titrations, samples were prepared by diluting 4 µL, 7 µL, 10 µL of 10^{-2} M of $CaCl_2$ to 10 mL by water to obtain the Ca^{2+} concentrations of 4×10^{-6} M, 7×10^{-6} M, and 10^{-5} M, respectively. Ca^{2+}-selective electrodes were used as endpoint detectors and Ca^{2+}-selective emulsion as titration reagent.

For potentiometric lead titration, the samples were prepared by adding 30 µL, 90 µL, 180 µL of 10^{-4} M $Pb(NO_3)_2$ to 30 mL water to obtain the Pb^{2+} concentrations 10^{-7} M, 3×10^{-7} M, and 6×10^{-7} M, respectively. Pb^{2+}-selective electrodes were used as endpoint detectors and Pb^{2+}-selective emulsion as titration reagents.

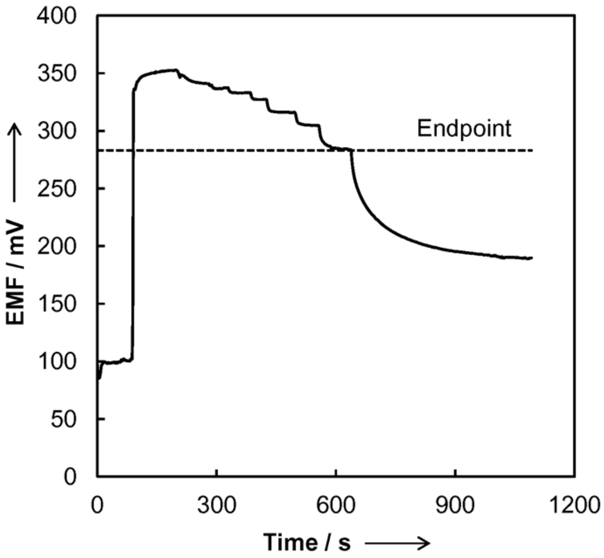

Fig. S1 Potentiometric titration curve for 7×10^{-6} M of Ca^{2+} in 10 mL non-buffered water. The volumes of the added calcium selective emulsion were 200 µL, 4 × 100 µL, 50 µL, 2 × 34 µL respectively. The concentration of the ion exchanger KTFPB in the calcium selective emulsion stock solution was 2.05×10^{-4} M.The endpoint appeared at 684 µL. The amount of the KTFPB at the endpoint was 140 nano mole.The response time is less than 1 min before the endpoint, and mainly dictated by the response time of the ion-selective electrode used for the detection.

1 Y. Qin, S. Peper and E. Bakker, *Electroanalysis*, 2002, **14**, 1375.