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Advancing Schwarzenbach's Complexometry: Nano-scale Titration Reagents Based on Heterogeneous Reactions

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Gerold Schwarzenbach's treatise on complexometric titrations established that for a titration reagent to be successful, the complexation reaction must be rapid, proceed stoichiometrically, and must be accompanied by a large change in free energy. The model reagent for this methodology has of course been EDTA, which forms stable complexes of a defined 1:1 stoichiometry with a wide range of metal ions. Chelating agents must be water soluble, and the associated ionizable groups necessitate a careful control of pH.

Our group recently introduced colloidal titration reagents that may dramatically increase the available chemical toolbox, alleviate the need for pH control and eliminate the requirement of a defined and singular reaction stoichiometry. The principle of this nanoscale reagent is shown in Fig. 1. The hydrophobic core of the suspended particles is doped with a lipophilic ion-exchanger and a chemical receptor molecule (ionophore) known from electrochemical and optical ion sensors. The ion of interest will spontaneously ion-exchange with the counter ion initially

present in the particle core. This extraction is driven by the lipophilicity difference between the two ions and the ion-receptor binding energy. For a sufficient molar excess of receptor, the binding capacity is dictated by the ion-exchanger concentration, and a fixed complex stoichiometry is no longer required. The receptors do not need to be water soluble and therefore do not require protonatable groups.

Fig. 2 demonstrates the titration of two different water samples using calcium-selective colloidal suspensions doped with cation-exchanger and a calcium-selective receptor. The titration was performed without pH control (titration with EDTA requires pH 10), detecting pCa with a calcium-selective electrode. The observed concentrations (5.2 ± 0.1 mM for Swiss Alpina and 2.1 ± 0.1 mM for Evian) agree quantitatively with the expected calcium levels (5.2 mM and 2.0 mM). The nanosphere suspensions are clear to the eye, simple to fabricate, and have been found stable for a number of weeks. Doping with different reagents will allow one to obtain binding affinities and selectivities that have been very difficult to achieve so far with traditional homogeneous reagents.

In conclusion, nanoscale titration reagents that work on the basis of extraction and complexation equilibria may overcome numerous limits imposed by water-soluble chelators that work in homogeneous phase.

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References

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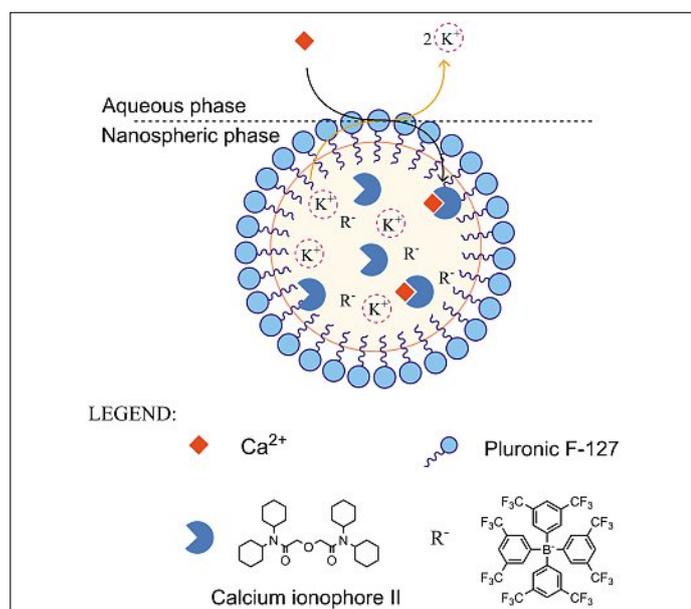


Fig. 1. Ion-selective nanospheres as complexing agent and structures of the compounds used in this work.

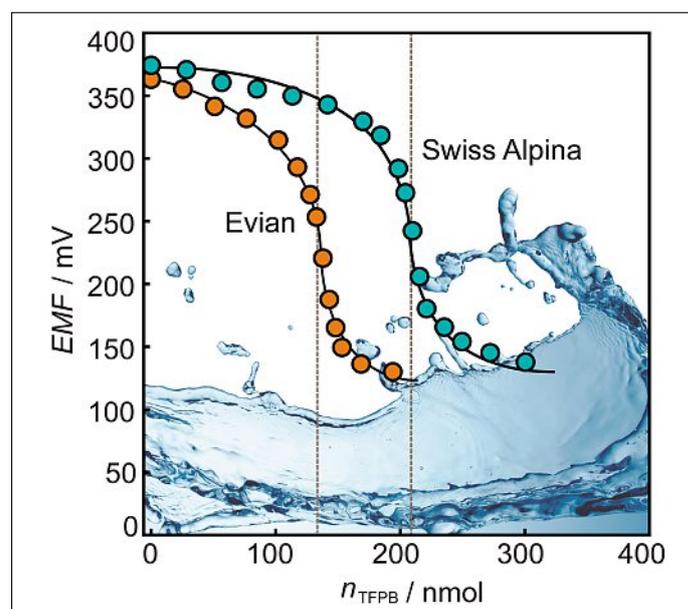


Fig. 2. Titration of Ca²⁺ in diluted mineral water Evian® and Swiss Alpina®, detection by calcium-sensitive electrode.

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