Investigation of nucleation processes with automated titrators

Using ion-selective electrodes to monitor free ion activity in a precursor solution

Summary

Controlling the nucleation processes of a material can improve the quality of the final product and size distribution of its particles. As material properties can vary depending on the particle sizes (*cf.* quantum confinement), understanding and monitoring the formation process is beneficial for manufacturers. Using an automated titrator allows deeper insight into some of these events, helping to gain more control over a complex process which affects the properties of the finished material.

The monitored graph is related to the LaMer model, a kinetically controlled formation from a supersaturated precursor solution which undergoes nuclei formation. It is possible to monitor the solubility product, nucleation events, and crystal growth. Metrohm provides the required sensors and dosing components to investigate the ideal conditions for investigation, synthesis, and process control purposes. This Application Note covers the formation of calcium carbonate from solution.

Configuration

2.907.0020 - 907 Titrando
High-end titrator for potentiometric and volumetric Karl Fischer titration with two measuring interfaces and Dosino dosing units. up to four dosing device systems of the 800 Dosino type; dynamic (DET), monotonic (MET) and endpoint titration (SET), enzymatic and pH-STAT titrations (STAT), Karl Fischer titration (KFT); "iTrode" intelligent electrodes; Measurement with ion-selective electrodes (MEAS CONC); Dosing functions with monitoring, liquid handling; four MSB connectors for additional stirrers or dosing device systems; USB connector; For use with OMNIS Software, tiamo software, or Touch Control; Complies with GMP/GLP and FDA regulations such as 21 CFR Part 11, if required;

2.906.0020 - 906 Titrando
High-end titrator for potentiometric and volumetric Karl Fischer titration with two measuring interfaces and Dosino dosing units. built-in buret drive; dynamic (DET), monotonic (MET) and endpoint titration (SET), enzymatic and pH-STAT titrations (STAT), Karl Fischer titration (KFT); Measurement with ion-selective electrodes (MEAS CONC); Dosing functions with monitoring, liquid handling; four MSB connectors; two galvanically isolated measuring interfaces; USB connector; For use with OMNIS Software, tiamo software, or Touch Control; Complies with GMP/GLP and FDA regulations such as 21 CFR Part 11, if required;

2.902.0010 - 902 Titrando
High-end potentiometric titrator for endpoint titration (SET), as well as enzymatic and pH-STAT titrations (STAT) with one measuring interface. up to four dosing device systems of the 800 Dosino type; Dosing functions with monitoring, liquid handling and tandem dosing; four MSB connectors for additional stirrers or dosing device systems; can be supplemented with one additional measuring interface; USB connector; For use with OMNIS Software, tiamo software, or Touch Control; Complies with GMP/GLP and FDA regulations such as 21 CFR Part 11, if required;

2.1001.0020 - OMNIS Titrator with magnetic stirrer, without function license

Innovative, modular potentiometric OMNIS Titrator for stand-alone operation or as the core of an OMNIS titration system. Thanks to 3S Liquid Adapter technology, handling chemicals is more secure than ever before. The titrator can be freely configured with measuring modules and cylinder units and can have a stirrer added as needed. Thanks to various software function licenses, various measuring modes and functionalities are possible. Control via PC or local network; Connection option for up to four additional titration or dosing modules for additional applications or auxiliary solutions; Connection option for one rod stirrer; Various cylinder sizes available: 5, 10, 20 or 50 mL; Liquid Adapter with 3S technology: Secure handling of chemicals, automatic transfer of the original reagent data of the manufacturerMeasuring modes and software options:; Endpoint titration: "Basic" function license; Endpoint and equivalence point titration (monotonic/dynamic): "Advanced" function license; Endpoint and equivalence point titration (monotonic/dynamic) with parallel titration: "Professional" function license;

6.00502.300 - Combined dCa ISE

Digital, combined calcium-selective electrode for OMNIS. This ISE is suitable for: Ion measurements of Ca2+ (1*10-7 to 1 mol/L) in aqueous solutions; Complexometric (back) titrations (e.g., determination of water hardness); Thanks to a robust/break-proof plastic shaft made of propylene and an impact protection for the polymer membrane, this sensor is mechanically very resistant.The reference electrolyte used is c(KCl) = 3 mol/L.dTrodes can be used on OMNIS Titrators.

6.0502.170 - Ion-selective electrode, Pb
Lead-selective electrode with crystal membrane.This ISE has to be used in combination with a reference electrode and is suitable for: ion measurements of Pb2+ (10-6 to 0.1 mol/L); ion measurements in small sample volumes (minimum immersion depth 1 mm); titrations (e.g., sulfate determination with lead nitrate); Thanks to the robust/break-proof plastic shaft made of EP, this sensor is mechanically very resistant.The polishing set supplied enables easy cleaning and renewing of the electrode surface.

6.0259.100 - Unitrode
Combined pH electrode for pH titrations. This electrode is particularly suitable:for pH titrations in difficult, viscous, or alkaline samples; at elevated temperatures; The fixed ground-joint diaphragm is insensitive to contamination.Reference electrolyte: c(KCl) = 3 mol/L, storage in storage solution.Alternatively: reference electrolyte for measurements at T>80°C: Idrolyte, storage in Idrolyte.

Sample and Sample Preparation

It is recommended to already have the solution and one component of the precursor prepared and to add the measured ion via a Metrohm dosing device. Sensor calibration and preconditioning depends on the system used for the investigation.

Experimental

Sensors and titrant solutions are used accordingly depending on the material and conditions to be investigated. As an example, the formation of calcium carbonate was examined. An OMNIS titrator was used in combination with OMNIS dosing modules (**Figure 1**) and a 902 Titrando. A carbonate solution was placed in a titration beaker and the pH was adjusted to 11 with a SET pH titration. After pH 11 was reached, a calcium chloride solution was added while the free Ca^{2+} concentration was measured in a MET U titration. Concurrently, a MEAS U with the Optrode was executed to monitor the qualitative transmittance of the solution. The pH of the solution was held at a static level with the STAT pH command executed via the 902 Titrando. For screening and optimizing parameters, a sample robot can be applied to increase sample throughput.

Figure 1. OMNIS Titrator with an OMNIS Dosing Module and an OMNIS sample robot S.

Results

The observation of calcium carbonate formation is shown in **Figure 2**. At the beginning, the potential without any calcium ions is displayed. Calcium is added at defined intervals into the carbonate-containing solution while the Ca^{2+} ion potential is monitored. The obtained U/t resp. U/V curve is related to the LaMer diagram with its different stages. At the beginning, an undersaturated solution is present without any solid phase formed (I). The potential increases due to added calcium ions, continuing to increase until nucleation takes place (II) and $CaCO_3$ forms. The transmittance (shown in orange) decreases dramatically once enough stable particles are formed. After the formation of stable particles, the calcium ion concentration in the solution decreases due to particle growth (III) and settles into a potential plateau. The potential at the plateau corresponds to a defined calcium ion concentration. This concentration equals the solubility product of $CaCO_3$ at the defined reaction conditions.

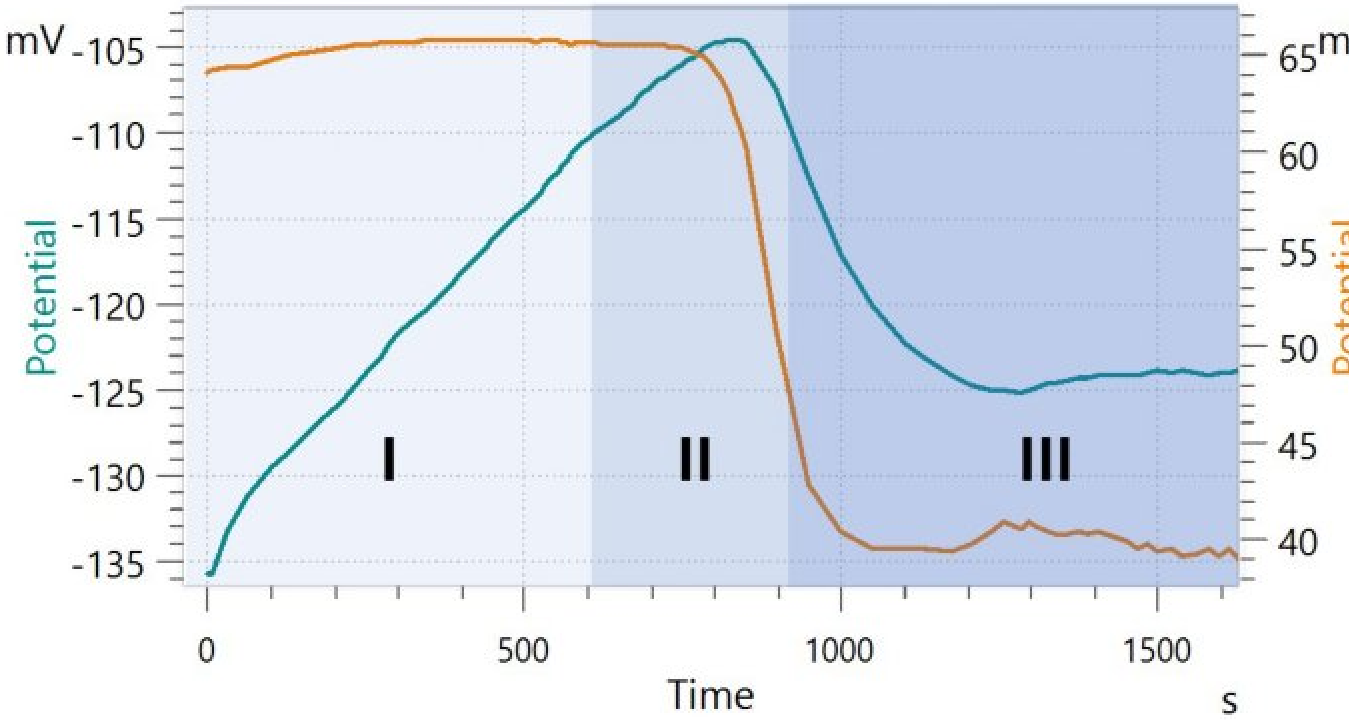

Figure 2. Example curve for calcium carbonate formation. In green is the potential of the free calcium ions measured with the combined Ca ion-selective electrode, and in orange, the potential measured with the Optrode. The experiment was carried out at pH 11. The colored phases describe the prenucleation phase (I), nucleation (II), and particle growth (III).

Both curves, calcium potential and transmittance potential, can be fused together with the COLLECT command and can be displayed in one graph.

Conclusion

Metrohm instruments provide superior performance for investigation of nucleation processes in various fields (e.g., materials science, biomineralization, pharmaceuticals, and geology). Different ion-selective electrodes can be applied including calcium, lead, copper, and much more.

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