Jungbunzlauer

From nature to ingredients®

facts

Effective chelation with Citrates and Gluconates

Introduction

Chelating agents are used in several different industrial fields, including home and personal care, food and beverages, and even pharmaceuticals, where the presence of metal ions might negatively impact the application. By binding metal ions, chelating agents prevent them interfering with desired reactions. Chelators also play a key role in the water softening process, where they remove insoluble deposits or prevent them from occurring in the first place.[1] In home care applications, chelating agents improve the effectiveness of surfactants by hindering the formation of insoluble salts. In the food and beverages industry for instance, chelating agents can prevent metallic or rancid off-tastes, which might be caused by metals present in the matrix.

It is estimated that by 2022 the annual global demand for chelating agents will reach 4.34 million tonnes, with the detergents and cleaners industry accounting for by far the biggest share of this volume figure.[2] Applications include washing powder, dishwashing detergents, industrial and institutional (I&I) cleaners, as well as household cleaner products. Currently, phosphates, especially sodium tripolyphosphate (STPP), and ethylenediaminetetraacetic acid (EDTA) derivates remain the most commonly used chelating agents globally.[2] However, many producers are trying to avoid the use of these chelators, since their excessive release into water increases the discharge of nutrients as well as complexes with low biodegradability. The demand for nontoxic ingredients in personal and home care products is also strong and growing. As a result, the search is on for ecologically and environmentally friendly ingredients for home care applications.

Jungbunzlauer's trisodium citrate and sodium gluconate are manufactured by fermentation of renewable raw materials, such as carbohydrates from corn. With their excellent chelating properties, trisodium citrate and sodium gluconate have proven to be viable bio-based alternatives. Both these Jungbunzlauer ingredients are readily biodegradable by many organisms not only under aerobic conditions, but also under anaerobic wastewater treatment conditions and in the natural environment. The fermentation-based manufacturing process from renewable raw materials together with good biodegradability make these two Jungbunzlauer ingredients sustainable options to replace traditional chelating agents. In addition, both sodium gluconate and trisodium citrate are ECOCERT approved as raw materials of 100% natural origin for use in detergents.

The chelating performance of Jungbunzlauer's TSA and SG vs. EDTA

The chelating capacity of the Jungbunzlauer products trisodium citrate anhydrous (TSA) and sodium gluconate (SG) as compared to EDTA was determined in a pH range of 10 to 13 and at 21°C and 40°C by precipitation titration. The higher temperature is relevant for home care applications such as dishwashing and laundry products.

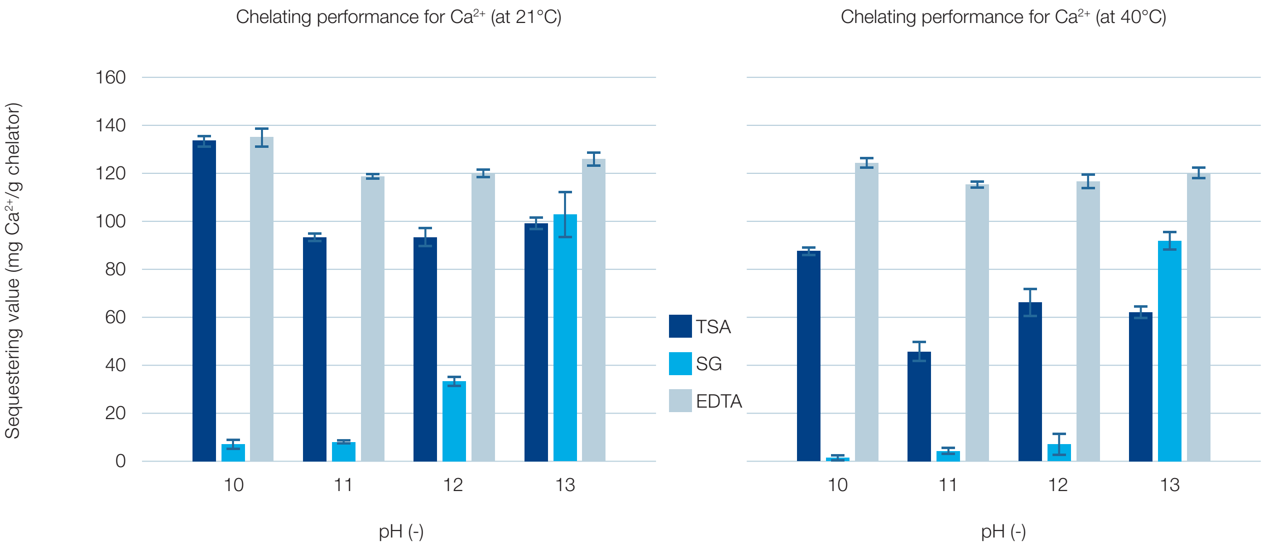
The method is based on the difference in solubility between the metal complexes formed by the chelators and the added counterions.[3] Performance was tested by adding the chelating agent and a solution of either carbonate or hydroxide ions as counterions to a beaker. Ammonium chloride was added as a buffer system. After adjusting the temperature by means of a heating unit and the pH value using sodium hydroxide, the titrant solution was slowly titrated into the beaker. Analysis was performed using the TitroLine® M7000 with an OptiLine® 6 optrode (Xylem Analytics Germany Sales GmbH & Co. KG). Further method details are available on request. Initially the solution was clear. The chelating agent, being the stronger ion, was able to form complexes with the available metal ions. However, its chelating capacity was limited. When more metal ions were added, the chelating agent was no longer able to bind them. The free metal ions were then available to form insoluble complexes with the counterions. The precipitation starting point was detected using an electrode at a wavelength of 625 nm.

This article evaluates the performance of the chelators in relation to calcium, magnesium and copper ions. The figures below show results for chelating capacity (mg metal ions per g chelating agent) dependent on pH value. The different chelating agents are classified by colour.

Sequestering values for calcium ions

The chelating performance for calcium ions was analysed using carbonate as the counterion (see figure 1), since this is especially relevant for home care applications. Measurements were carried out using a calcium acetate solution as the calcium source. The results for chelating capacity are shown in figure 1, with the left-hand column showing results at a temperature of 21°C, while the right shows results with an elevated temperature of 40°C.

Figure 1: Chelating performance for calcium ions (in mg Ca^{2+} per g chelator) at 21°C (left) and 40°C (right) at varied pH values (10–13) for TSA, SG and EDTA (n = 4).

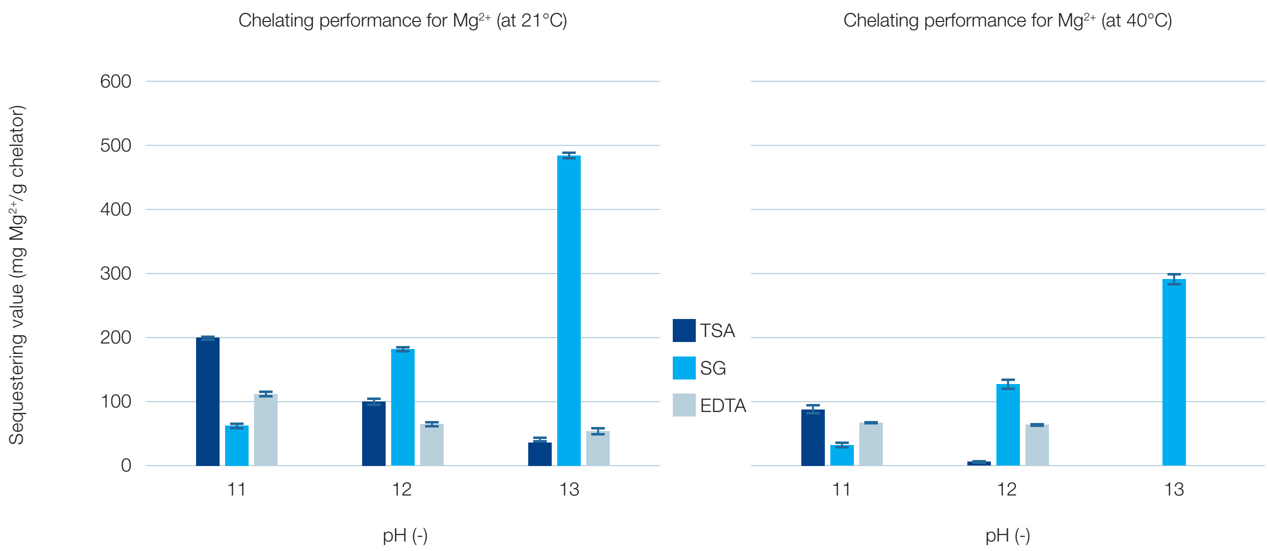


At 21°C the chelating performance of all agents is pH dependent. At pH 10 TSA and EDTA possess a comparable chelating capacity of around 130 mg calcium per g chelator, which enables one-to-one replacements for more sustainable formulations. To replace EDTA in a formulation at pH 13, the amount of TSA should be increased by about 30 wt%. Adding the optimum amount of chelating agent reduces the formation of calcium carbonate deposits, meaning less greying of clothes and dishes.[2] The chelating performance of SG improves rapidly when pH values are raised. Adjusting the pH value from 12 to 13 causes its chelating capacity to increase threefold. Similar trends can be observed at 40°C, although overall the chelating performance declines when the temperature is raised. By preventing soaps and detergents from reacting with the mineral deposits in hard water, these environmentally friendly chelators stop scum formation, improve cleaning performance at low temperatures and effectively shorten washing cycles.[1]

Sequestering values for magnesium ions

After calcium, the most common metal ions in tap water are usually magnesium. The method used for precipitation titration of magnesium was similar to that for calcium, but with magnesium acetate solution as titrant and hydroxide ions as counterions. Figure 2 shows the chelating performance for Mg^{2+} in a pH range of 11 to 13.

Figure 2: Chelating performance for magnesium ions (in mg Mg^{2+} per g chelator) at 21°C (left) and 40°C (right) at varied pH values (11—13) for TSA, SG and EDTA (n = 4).



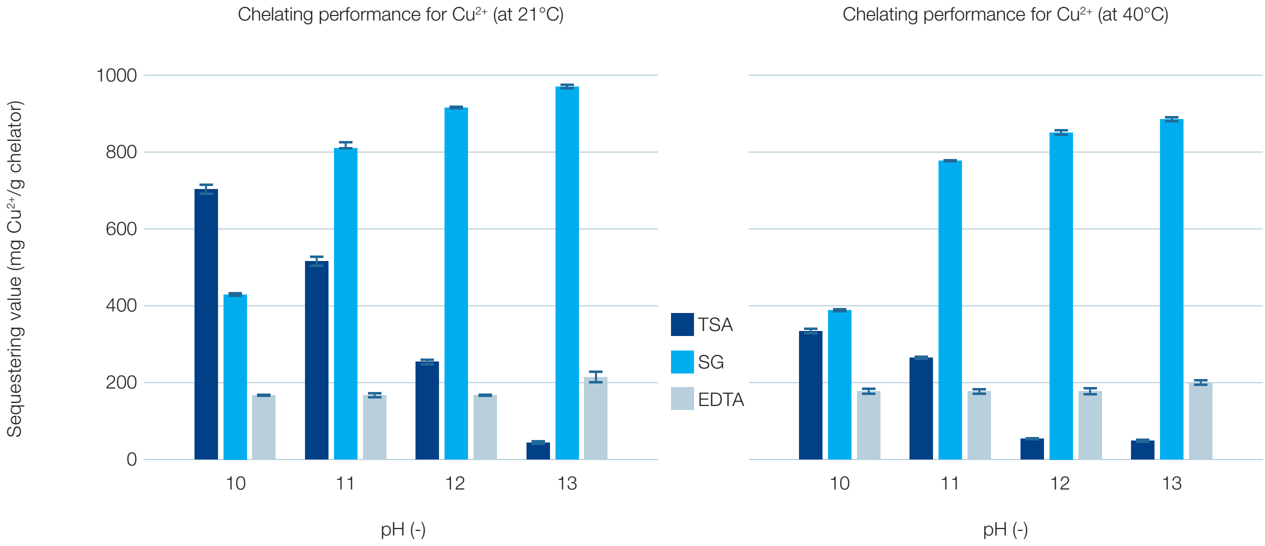
Overall, the chelating performance trends for magnesium ions at 21°C are similar to those for calcium ions. At pH 11 the chelating capacity of TSA is about 200 mg Mg^{2+} per g chelator, which is almost double the building performance of EDTA, i.e. only half as much TSA as EDTA is needed for effective inhibition of laundry greying. At higher pH values, SG shows a particularly impressive increase in chelating capacity. One gram sodium gluconate can chelate about 485 mg Mg^{2+} at pH 13, which is nine times as much as EDTA. At the higher temperature the trends were also comparable. TSA and EDTA both lose about a quarter of their chelating capacity at the higher temperature, resulting in its complete loss at pH 13, whereas SG continues to demonstrate a high sequestering value. Hence, the capacity of gluconates and citrates to chelate magnesium ions is comparable with or even better than EDTA, making them good alternatives to the chelators currently in common use.

Sequestering values for copper ions

Chelating agents have the ability to complex transition metals like copper and iron, as well as calcium and magnesium ions. This behaviour improves the shelf life of the product, for example by optimising colour stability and delaying the oxidative degradation of oils and perfumes.[4] Additionally, building complexes with free trace metal ions protects the oxidising agents in laundry formulations, assuring their performance.[1]

A copper sulfate solution was used as the metal ion source to determine chelating capacity for copper. Because of the ability of Cu^{2+} to form various complexes, the selection of a buffer system was not trivial.[3] It was therefore decided to adjust the pH value by adding sodium hydroxide alone. The available copper ions formed blue to turquoise complexes with hydroxide ions. The wavelength used to detect the precipitate was 470 nm.

Figure 3: Chelating performance for copper ions (in mg Cu^{2+} per g chelator) at 21°C (left) and 40°C (right) at varied pH values (10 – 13) for TSA, SG and EDTA (n = 4).



The sequestering capacity for copper ions, shown in figure 3, is greatly increased with TSA and SG as compared to EDTA. At pH 10 the building capacity of TSA (about 700 mg per g chelator) is more than four times greater than that of EDTA. With higher pH values the trends are similar to the results for calcium and magnesium. For an I&I cleaning application in alkaline conditions (pH 13) SG has by far the best building performance, being about 4.5 times as effective as EDTA. Building water-soluble complexes with trace metal ions and citrates in laundry applications improves stain removal, especially for difficult stains such as red wine.[5] At the elevated temperature the chelating capacity of TSA is reduced by half, whereas the values of EDTA and SG are considerably less temperature-dependent. In addition to its important role in the cleaning process, complexing multivalent metal ions renders them unavailable to microorganisms. As a result these microorganisms cannot maintain their barriers and are therefore more vulnerable to biocides.[6] This improves the shelf life of liquid formulations.

Summary

Citrates and gluconates are effective, environmentally friendly chelating agents. With pH values in the higher range their building capacity is comparable to or even greater than the commonly used chelating agent EDTA. Effective complexation of calcium and magnesium ions with trisodium citrate enables EDTA replacement, notably at pH values 10 and 11. Because trisodium citrate and in particular sodium gluconate are very good at sequestering trace metals such as copper they have the capacity to boost stain removal and prolong the shelf life of the formulation.

Furthermore, trisodium citrate satisfies current demands for biodegradable ingredients and low-temperature cleaning, making it well suited to replace EDTA in home care applications. In alkaline cleaning formulations such as I&I applications sodium gluconate very effectively complexes metal ions, especially copper.

References

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About Jungbunzlauer

Jungbunzlauer is one of the world's leading producers of biodegradable ingredients of natural origin. We enable our customers to manufacture healthier, safer, tastier and more sustainable products. Thanks to continuous investment, state-of-the-art manufacturing processes and comprehensive quality management, we are able to provide outstanding product quality.

Our mission "From nature to ingredients®" commits us to protecting people and their environment.

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