

# Adsorption of Carboxylate Anions on a $\text{CaCO}_3$ Surface

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The adsorption behavior of benzoate, citrate, tartrate and glutamate on calcite dispersed in water was studied. At r. t. and  $\text{pH} = 9$ , the molar amount of substrate adsorbed decreases with increasing number of carboxylic groups in the molecule. Thus, monofunctional benzoate adsorbs in significantly higher molar amounts than trifunctional citrate. A more alkaline environment ( $\text{pH} = 12.5$ ) has almost no effect on the adsorption behavior whereas a temperature increase, particularly from 40 to 60 °C, results in notably lower adsorbed amounts except for benzoate. Enthalpy changes determined by applying a modified Clausius-Clapeyron equation indicate a slightly exothermic benzoate adsorption process, whereas adsorption of citrate, tartrate and glutamate represents an endothermic, entropy-driven process. Zeta potential measurements conducted with highly concentrated  $\text{CaCO}_3$  suspensions (water/ $\text{CaCO}_3 = 0.413$ ) containing 0–100 mmol substrate/ $\text{m}^2$  confirm that the adsorption of substrates with a higher number of carboxylic groups and a higher anionic charge results in a particularly negative surface charge on  $\text{CaCO}_3$ .

**Key words:** Adsorption, Enthalpy, Carboxylic Acids, Zeta Potential, Calcite

## Introduction

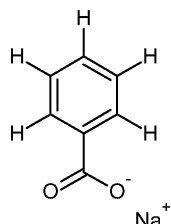
The surface chemistry of calcium carbonate is rather complex. It is generally accepted that the mineral exhibits a basic character in nonaqueous systems, while a surface charge exists in aqueous media [1]. The surface charge is caused by the dissolution of ions from the  $\text{CaCO}_3$  surface. At  $\text{pH} \leq 9$ ,  $\text{Ca}^{2+}$ ,  $\text{HCO}_3^-$  and  $\text{OH}^-$  ions were found in the aqueous phase. At  $\text{pH}$  above 9,  $\text{CO}_3^{2-}$  appears in addition to these ions and reaches the highest concentration of all ions present [2]. Thus, the partial dissolution of calcium carbonate affects its surface charge, its colloidal properties and its interaction with other substrates [3]. The results of numerous investigations on the adsorption of small organic anions such as salicylate and of succinic, phthalic and maleic acid on  $\text{CaCO}_3$  have been published [4,5]. Surface complexation occurs between the carboxylate groups of these molecules and hydrated calcium atoms located on the  $\text{CaCO}_3$  surface exposed to the liquid phase [6]. 10 mM aqueous solutions of succinate, phthalate or maleate strongly inhibit the dissolution of calcite [5], whereas salicylate adsorption causes ligand-promoted dissolution of gibbsite [4c]. By comparing the adsorption of phthalic, sal-

icylic and *p*-hydroxybenzoic acid on an  $\alpha\text{-Fe}_2\text{O}_3$  surface at  $\text{pH}$  3–11, Gu *et al.* [7] have found that two adjacent  $-\text{COOH}$  groups result in much higher adsorption than a  $-\text{COOH}$  and an  $-\text{OH}$  group in *ortho* or *para* position. Similarly, Das *et al.* [8] have shown that on  $\alpha$ -alumina, more phthalate is adsorbed than benzoate because of the two adjacent  $-\text{COOH}$  groups in the former. Consequently, for small organic anions on a given positive surface, the adsorbed amount and the ratio between adsorbed and dissolved substrate (adsorption equilibrium) generally depend on the type and number of the functional groups responsible for adsorption and the stereochemistry of the substrate molecule.

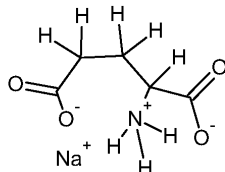
The aim of the present investigation was to elucidate the interaction of small carboxylate anions with the  $\text{CaCO}_3$  surface. The four substrates used in this study are shown in Fig. 1. Benzoate, tartrate and citrate were chosen for this study because of their carboxylate groups and their widespread use to retard cement hydration in concrete and dry-mix mortars containing limestone powder. They represent mono-, di- and tri-carboxylates, which are known to form Ca complexes in aqueous solution. The substrate which interacts with the  $\text{CaCO}_3$  surface greatly depends on the  $\text{pH}$  value.

Table 1.  $pK$  Values of the four carboxylic acids used in the study.

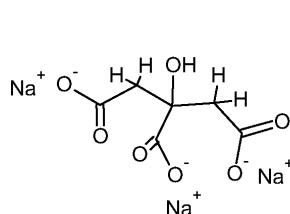
Organic acids	$pK_1$	$pK_2$	$pK_3$
Benzoic	4.0	–	–
Citric	2.9	4.4	5.7
Tartaric	2.8	4.0	–
Glutamic	2.2	4.2	–



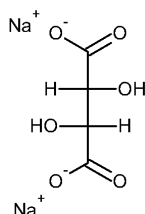
sodium benzoate



sodium L-glutamate



tri-sodium citrate



disodium L-tartrate

Fig. 1. Mono- and polycarboxylates used in the study.

The  $pK$  values of the carboxylic acids studied here are shown in Table 1 [9].

For benzoate, three calcium complexes have been reported, namely  $[\text{Ca}(\text{C}_6\text{H}_5\text{COO})_2] \cdot 3\text{H}_2\text{O}$  (from neutral solution),  $[\text{Ca}(\text{C}_6\text{H}_5\text{COO})_2](\text{C}_6\text{H}_5\text{COO})_{0.5} \cdot 2\text{H}_2\text{O}$  (from acidic solution) [10] and  $[\text{Ca}(\text{C}_6\text{H}_5\text{COO})_2]$  (from hydrothermal synthesis) [11]. Senkovska and Thewalt determined the crystal structure of  $\{[\text{Ca}(\text{C}_7\text{H}_5\text{O}_2)(\text{H}_2\text{O})_3](\text{C}_7\text{H}_5\text{O}_2)\}_n$ , where the Ca atom is eight-coordinated by four carboxylate oxygen atoms and four water molecules. The structure consists of polymeric  $\{[\text{Ca}(\text{C}_6\text{H}_5\text{COO})(\text{H}_2\text{O})_3]^+\}_\infty$  chains alternating with layers of uncoordinated  $\text{C}_6\text{H}_5\text{COO}^-$  anions [12]. Calcium benzoate hydrates (trihydrate and monohydrate) were also described by Terakita and Byrn [13].

Ca tartrate complexes were also established. The crystal structure of calcium tartrate tetrahydrate ( $\text{CaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$ ) was described by Ambady [14], where Ca is involved in the formation of planar bidentate chelate rings, with all four carboxyl oxygen atoms lying in proximity to either water molecules or hy-

droxyl groups at distances which suggest hydrogen-bond formation. Studies of concentration and thermodynamic stability constants proved that at pH between 5.5 and 6.5, the neutral Ca tartrate complex exists, while at pH = 3.5–4.5, both calcium tartrate and  $[\text{calcium}(\text{Htartrate}^-)]^+$  are found [15].

Citric acid possesses even four acidic protons. Its  $-\text{OH}$  group is deprotonated at pH above 11 [16]. Citrate forms various chelates in the presence of Ca ions [17]. According to [18], these chelates are converted into thermodynamically more stable, but less soluble Ca complexes.

Glutamate, because of its additional N-functionality, was expected to adsorb differently than organic species without nitrogen. Composition and structure of calcium glutamate complexes were extensively investigated. At pH = 10, trigonal crystals of calcium L-glutamate trihydrate ( $\text{CaC}_5\text{H}_7\text{NO}_4 \cdot 3\text{H}_2\text{O}$ ) are formed where each glutamate ion chelates three symmetry-related Ca ions, two through the four oxygen atoms of the carboxyl groups and the third through its nitrogen atom in concert with one of its carboxyl oxygen atoms [19]. Crystals of calcium di-L-glutamate tetrahydrate  $[\text{Ca}(\text{C}_5\text{H}_8\text{NO}_4)_2 \cdot 4\text{H}_2\text{O}]$ , formed at pH = 7, were found to have the Ca ion coordinated to two water molecules and to the carboxyl oxygen atoms of two glutamates, where each glutamate serves as a unidentate ligand [20].

Thus, it is evident that the substrates obtained from the four carboxylic acids at different pH values can interact in various ways with the surface of  $\text{CaCO}_3$ .

In our study, adsorption isotherms, adsorption enthalpies as well as zeta potentials of  $\text{CaCO}_3$  suspensions containing these anions were determined at pH = 9 (native pH of the  $\text{CaCO}_3$  slurry) and pH = 12.5, to investigate the effect of pH and the corresponding anionic substrate on the interaction with the  $\text{CaCO}_3$  surface.

## Experimental Section

The experiments were performed with aqueous suspensions of  $\text{CaCO}_3$  (SCHAEFER Precal 18, Schaefer Kalk GmbH & Co K G, Diez, Germany). Its medium particle size  $D_{50}$  was  $12.58 \mu\text{m}$  and the specific surface area was  $0.283 \text{ m}^2 \text{ g}^{-1}$  (BET method) and  $0.345 \text{ m}^2 \text{ g}^{-1}$  (BLAINE method), respectively. The density was found to be  $2.688 \text{ g cm}^{-3}$ . Sodium benzoate, di-sodium L-tartrate dihydrate, tri-sodium citrate dihydrate and sodium L-glutamate monohydrate (all from Merck) were used without further purification.

Adsorption measurements on  $\text{CaCO}_3$  were carried out at 20, 40 and 60 °C by determining the unadsorbed organic carbon content in the centrifugate *via* a High TOC II analyzer (Elementar, Hanau, Germany). 0.1–5 % by weight of (bwo)  $\text{CaCO}_3$  of the organic salts was added to the aqueous  $\text{CaCO}_3$  suspension (water/ $\text{CaCO}_3$  ratio = 0.413) and mixed thoroughly with the help of a test tube shaker (VWR International, Darmstadt, Germany) for 1 min. The suspension was then centrifuged for 20 min at 8500 rpm. Adsorption measurements performed over 4 h confirmed that the state of equilibrium was fully attained after 2 min.

Zeta potential and conductivity of aqueous  $\text{CaCO}_3$  suspensions containing different concentrations of the substrates were measured at different pH using a Model DT-1200 Electro-acoustic Spectrometer (Dispersion Technology, Inc., New York, USA). The following mixing procedure was used to prepare the  $\text{CaCO}_3$  suspensions: 400 g of  $\text{CaCO}_3$  was added to 165.2 g of water within 1 min. This slurry was let sit for one more minute. Afterwards, the mixture was vigorously stirred for 2 min in a casserole with a spoon. Filtration gave the mother liquor for the measurement of the ionic background of the  $\text{CaCO}_3$  suspension which was subtracted from the zeta potential values of the  $\text{CaCO}_3$  slurries containing the organic substrates.

## Results and Discussion

### Adsorption

The adsorbed amounts of benzoate, tartrate, citrate and glutamate on the  $\text{CaCO}_3$  surface determined at dosages of 0.1–1.0 % bwo  $\text{CaCO}_3$  and at pH = 9 are shown in Fig. 2. It appears that the adsorbed molar amount of all organic substrates increases with dosage. Benzoate shows the heaviest adsorbed molar load and citrate the lowest one. The trifunctional citrate achieves compensation of the surface charge at lower dosages than two- or monofunctional carboxylates. No saturation points of adsorption were obtained at the dosages tested here. Zeta potential measurements described later showed that saturation points were reached at dosages of 10–20 mmol substrate/ $\text{m}^2$   $\text{CaCO}_3$  surface. The adsorbed molar amounts of tartrate and glutamate were nearly the same.

For calcium citrate, the ratio between the adsorbed and the total amount initially added has been reported to range from 19–52 %, depending on the dosage [21]. This is in good accord with our findings for trisodium citrate, which have shown that about 20 % of the citrate is adsorbed. Adsorption of disodium tartrate onto  $\text{CaCO}_3$  was found to correspond to a Type II isotherm [22]. In the vast majority of cases, physical

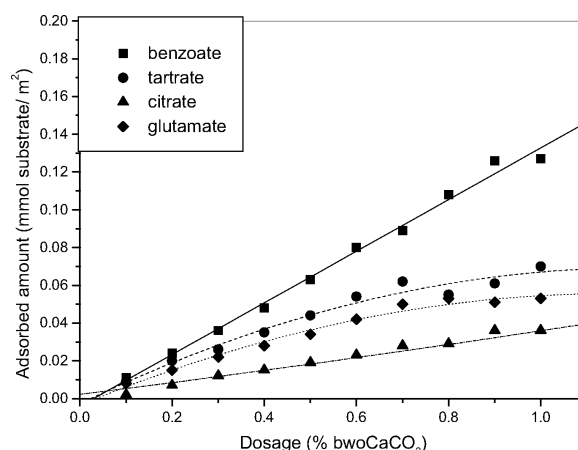


Fig. 2. Adsorbed molar amounts of benzoate, tartrate, citrate and glutamate on a  $\text{CaCO}_3$  surface at 20 °C and pH = 9 as a function of dosage.

adsorption gives rise to a Type II isotherm. In this case, only the forces between the adsorbent and the substrate (vertical interactions) are considered, whereas the forces between neighboring adsorbed molecules on the surface (horizontal interactions) are neglected. Interactions between adsorbed molecules must be taken into account when a layer is approaching the saturation point and the distance of the adsorbed molecules becomes small in relation to their size [22].

### Effect of pH on the adsorption behavior

To investigate the effect of pH on the adsorbed amount of substrate, the pH of the  $\text{CaCO}_3$  suspension was adjusted to 12.5 with NaOH. The substrate dosage added varied from 0.1 to 5 % bwo  $\text{CaCO}_3$ . The results are displayed in Fig. 3. Surprisingly, the adsorption appears to depend very little on the pH. An increase in pH to 12.5 causes only a slight increase in the amount of adsorbed benzoate, tartrate, citrate and glutamate. Interestingly, no saturation point for the adsorbed amount is reached even at concentrations as high as 5 % bwo  $\text{CaCO}_3$ .

### Effect of temperature on adsorption

At pH = 9, the effect of temperature on the adsorbed amount was investigated at 20, 40 and 60 °C. The results are presented in Figs. 4–7. It appears that, except for benzoate, an increase in temperature results in a decrease of the adsorbed amounts of the substrate. The decrease is particularly pronounced between 40

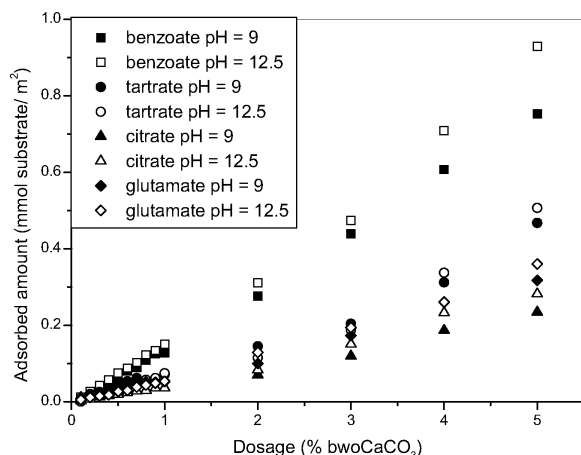


Fig. 3. Comparison of dosage-dependent adsorbed molar amounts of benzoate, tartrate, citrate and glutamate on a  $\text{CaCO}_3$  surface at pH = 9 and 12.5.

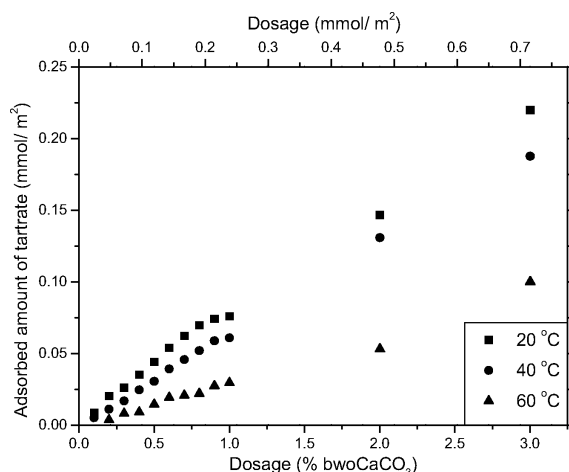


Fig. 5. Adsorbed molar amount of tartrate on  $\text{CaCO}_3$  at 20, 40 and 60 °C at pH = 9.

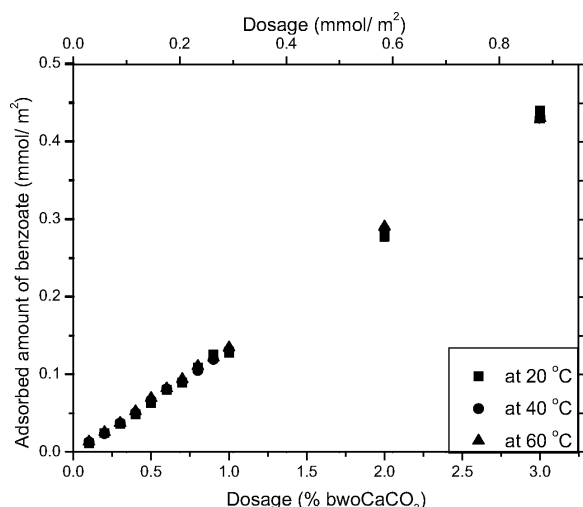


Fig. 4. Adsorbed molar amount of benzoate on  $\text{CaCO}_3$  at 20, 40 and 60 °C at pH = 9.

and 60 °C. Of all substrates, tartrate adsorption shows the strongest dependence on temperature. The adsorption of benzoate is not affected by the temperature variation.

Generally, the adsorption of ionic species on oppositely charged surfaces is thought to follow a two-step mechanism: First, adsorption occurs as a result of an electrostatic interaction by means of ion exchange, ion-pair formation, hydrogen bonding or complex formation on the surface, whereupon a first adsorption plateau is often reached. Secondly, increased adsorbent concentration may lead to the formation of a second

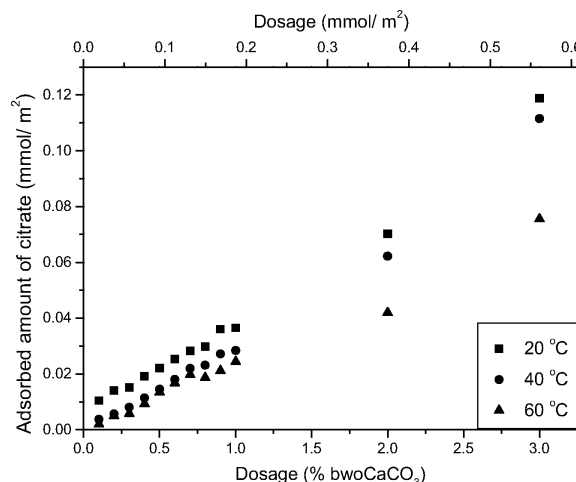


Fig. 6. Adsorbed molar amount of citrate on  $\text{CaCO}_3$  at 20, 40 and 60 °C at pH = 9.

adsorbed layer, resulting from substrate-substrate interactions. Formation of the second layer results in a reduction of the adsorption enthalpy and consequently in an increase of the system's entropy [3].

#### Enthalpy of adsorption on the $\text{CaCO}_3$ surface

Based upon the temperature dependence of the adsorbed amounts of substrate at pH = 9, the adsorption enthalpies were determined using the method of Peng *et al.* [23]. These authors calculated the enthalpy changes associated with adsorption processes based upon a modified Clausius-Clapeyron equation in which

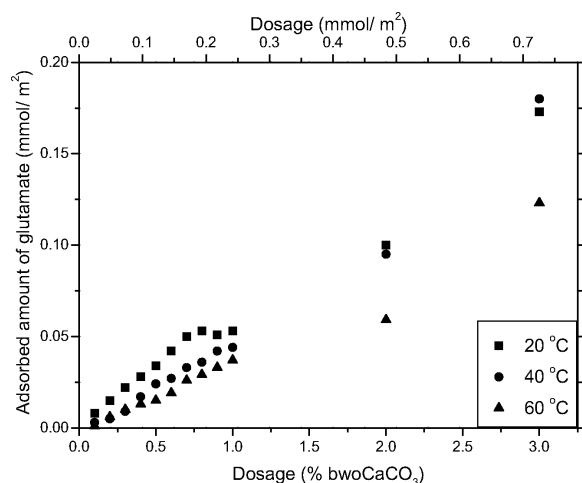


Fig. 7. Adsorbed molar amount of glutamate on CaCO<sub>3</sub> at 20, 40 and 60 °C at pH = 9.

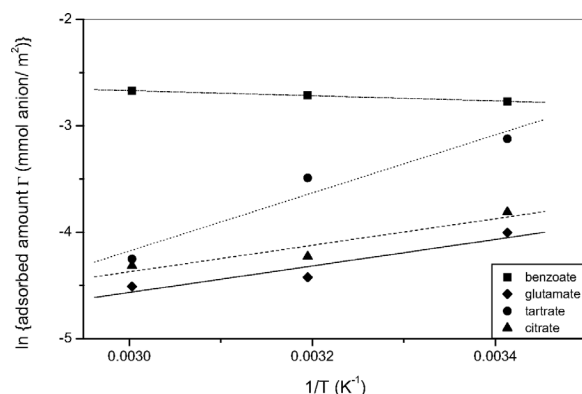


Fig. 8. Adsorbed amount of benzoate, glutamate, tartrate and citrate at a dosage of 0.5 % bwo CaCO<sub>3</sub> as a function of  $1/T$ .

the enthalpy of vaporization  $\Delta H_{\text{vap}}$  is substituted by the adsorption enthalpy  $\Delta H_{\text{ads}}$ , and the pressure  $P$  by the amount of adsorbed substrate  $\Gamma_{\text{ads}}$  (eq. (1)).

$$\Delta H_{\text{ads}}/R = (d \ln \{\Gamma_{\text{ads}}\} / d \{1/T\}) \quad (1)$$

Fig. 8 shows the plot of the temperature-dependent amount of adsorbed substrate for a dosage of 0.5 % bwo CaCO<sub>3</sub>. The slope of the curve ( $d \ln \{\text{adsorbed amount}\} / d \{1/T\}$ ) is equivalent to  $\Delta H_{\text{ads}}/R$  and was used to calculate the adsorption enthalpy  $\Delta H_{\text{ads}}$ .

Generally, the dosage-dependent enthalpy changes for adsorption of tartrate, citrate and glutamate can be expressed by the exponential eq. (2),

$$y = y_0 + A_1^* \exp(-x/t_1) \quad (2)$$

Table 2. Fitting parameters  $y_0$ ,  $A_1$ ,  $t_1$  and  $r^2$  for the temperature-dependent adsorption of the substrates shown in Fig. 8.

Substrate	$y_0$	$A_1$	$t_1$	$r^2$
Tartrate	$9.4 \pm 1.2$	$48.8 \pm 12.7$	$0.1 \pm 0.0$	0.878
Citrate	$16.6 \pm 2.1$	$47.0 \pm 17.1$	$0.3 \pm 0.1$	0.813
Glutamate	$7.8 \pm 3.0$	$27.2 \pm 5.5$	$0.4 \pm 0.2$	0.762

Table 3. Enthalpy change upon the adsorption of benzoate, tartrate, citrate and glutamate at 0.1–3 wt-% dosage on a CaCO<sub>3</sub> surface.

Dosage of substrate (%bwo CaCO <sub>3</sub> )	Adsorption enthalpy $\Delta H_{\text{ads}}$ (kJ mol <sup>-1</sup> )			
	Benzoate	Tartrate	Citrate	Glutamate
0.1	-3.5	7.2	34.5	33.2
0.2	-0.5	35.3	15.1	17.3
0.3	-0.6	35.3	19.6	23.6
0.4	-1.4	27.6	15.1	15.4
0.5	-2.0	16.1	10.4	22.7
0.6	-0.3	20.7	8.7	16.5
0.7	-0.9	22.1	7.4	13.8
0.8	-0.3	18.6	9.6	12.6
0.9	0.8	16.0	10.8	8.5
1.0	-1.1	17.4	8.2	7.4
2.0	-0.9	20.0	10.3	10.6
3.0	0.5	14.3	9.0	6.8

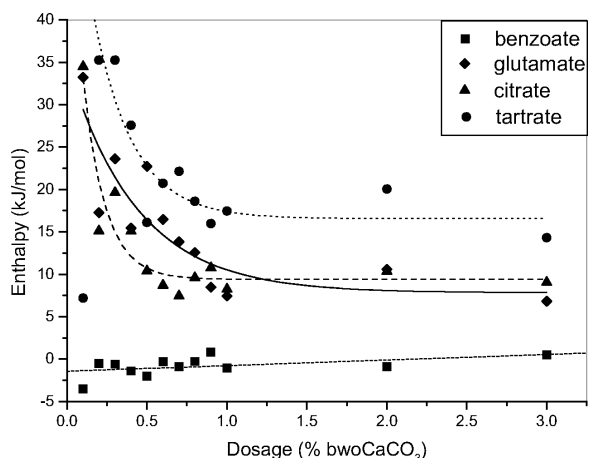


Fig. 9. Enthalpy change upon adsorption of various dosages of benzoate, tartrate, citrate and glutamate on CaCO<sub>3</sub>.

where  $x$  is the dose (in % bwo CaCO<sub>3</sub>),  $y$  is the adsorption enthalpy (in kJ/mol) and  $y_0$ ,  $A_1$  and  $t_1$  are constants of the exponential relationship. Table 2 shows the values of  $y_0$ ,  $A_1$  and  $t_1$  for tartrate, citrate and glutamate calculated from the results shown in Fig. 8;  $r^2$  is the correlation coefficient.

Employing this method, the enthalpy changes upon adsorption of benzoate, tartrate, citrate and glutamate on a CaCO<sub>3</sub> surface at pH = 9 and 0.1–3 % bwo CaCO<sub>3</sub> dosage were calculated. The results are listed

in Table 3 and presented in Fig. 9. It again appears that benzoate behaves quite differently from the other substrates. Its adsorption enthalpy is slightly exothermic ( $-1 \text{ kJ mol}^{-1}$ ) whereas the other substrates show highly endothermic enthalpies ( $7\text{--}35 \text{ kJ mol}^{-1}$ ) indicating entropy-driven processes. Tartrate exhibits the most endothermic adsorption enthalpy whereas glutamate and citrate show quite comparable enthalpies at all dosages. Benzoate's exothermic adsorption enthalpy is almost constant for various dosages while a sharp decrease of the endothermic adsorption enthalpy up to a dosage of *ca.* 1 % bwo  $\text{CaCO}_3$  is observed for the other substrates. It can be assumed that the decrease in adsorption enthalpy of citrate, tartrate and glutamate is caused by a change in the conformation of the anions adsorbed. The fundamental difference in the enthalpy values between benzoate and the other substrates may result from the greater flexibility of citrate, tartrate and glutamate anions. Upon adsorption, their entropy loss is significantly greater than for benzoate.

#### Zeta potential measurements

Zeta potential measurements were performed to determine the surface charge of the calcium carbonate particles in the presence of varying dosages of the substrates. Generally, charge, spatial arrangement and conformation play an important role in the adsorption behavior of the anions involved. Solvent, temperature and ionic strength can influence the structure and properties of the adsorbate. This is reflected by the zeta potential of the particles. Calcium carbonate particles suspended in water containing an organic salt form a Stern layer of adsorbed ions while hydrated ions remain in solution. Further organic molecules may be adsorbed on the Stern layer. As a consequence, a diffuse electric double layer (EDL) is formed around the particles. The concentration of ions oppositely charged to the Stern layer decreases exponentially with the distance from the  $\text{CaCO}_3$  particle. In the vast majority of previous zeta potential measurements, highly diluted suspensions with ratios water/ $\text{CaCO}_3 = 1$  to 1500 were used [24]. However, in many practical applications such as dry-mix mortars, highly concentrated  $\text{CaCO}_3$  suspensions with ratios water/ $\text{CaCO}_3 < 1$  are commonly used. Therefore, a  $\text{CaCO}_3$  suspension with the ratio water/ $\text{CaCO}_3 = 0.413$  was studied by using the electroacoustic method which allows to obtain results

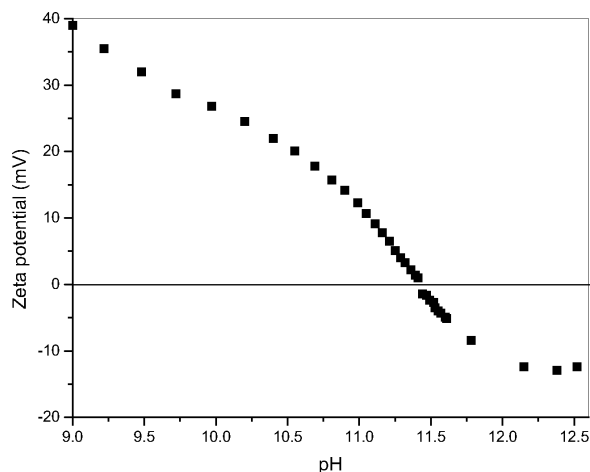


Fig. 10. Zeta potential of the  $\text{CaCO}_3$  suspension at pH = 9 to 12.5.

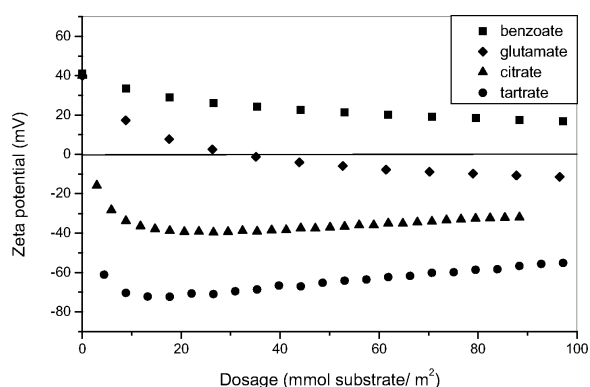


Fig. 11. Zeta potential of aqueous  $\text{CaCO}_3$  suspensions at pH = 9, treated with 0–100 mmol substrate/ $\text{m}^2$  of benzoate, tartrate, citrate and glutamate.

that correspond to practical conditions in building materials.

First, the zeta potential of the  $\text{CaCO}_3$  suspension was measured at pH = 9 to pH = 12.5 by adding dilute sodium hydroxide solution. According to Fig. 10, the zeta potential at pH = 9 is +40 mV. The surface potential decreases steeply to negative values as the pH of the suspension increases. This effect is caused by the adsorption of hydroxide ions on the initially positively charged surface. At pH = 12.5, the surface charge of  $\text{CaCO}_3$  is –15 mV and fairly stable because saturation of adsorption has been reached.

Secondly, the  $\text{CaCO}_3$  suspension (0.1–5 % bwo  $\text{CaCO}_3$ ) at pH = 9 was treated with benzoate, tartrate, citrate and glutamate. Addition of increasing amounts of substrate resulted in a decrease of the zeta poten-

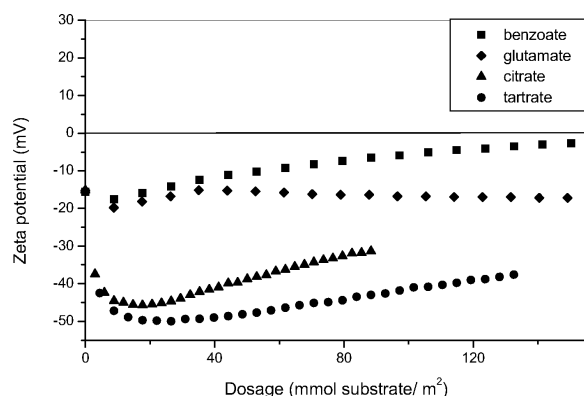


Fig. 12. Zeta potential of aqueous  $\text{CaCO}_3$  suspensions, treated with 0–140  $\text{mmol m}^{-2}$  of benzoate, tartrate, citrate and glutamate at pH = 12.5.

tial as shown in Fig. 11. The decrease is strongest for tartrate and less strong for citrate and glutamate. Benzoate shows the least change in zeta potential with dosage. For example, addition of 20  $\text{mmol m}^{-2}$  of benzoate decreases the zeta potential only to approximately +30 mV whereas the same amount of tartrate produces a zeta potential of about –70 mV.

At pH = 12.5 (Fig. 12), the zeta potential of the native  $\text{CaCO}_3$  suspension without further additives is –15 mV. In the case of benzoate, the potential decreases towards the isoelectric point with increasing dosage of the anion. Glutamate shows almost no effect of dosage on the zeta potential, whereas citrate as well as tartrate initially cause a sharp decline to highly negative zeta potential values. This effect can be explained by substitution of initially adsorbed hydroxyl anions on the  $\text{CaCO}_3$  surface. Correspondingly, an increase in pH caused by the desorbed  $\text{OH}^-$  ions was

observed. At higher concentrations, the zeta potentials of  $\text{CaCO}_3$  suspensions treated with citrate and tartrate become slightly less negative.

## Conclusion

The adsorption behavior of salts of carboxylic acids on  $\text{CaCO}_3$  is greatly influenced by the number of carboxylate functions in the molecule. High numbers of carboxylate groups require smaller molar amounts of the organic anion to achieve charge compensation on the  $\text{CaCO}_3$  surface, as shown by zeta potential measurements. The pH has a very slight effect on the adsorption behavior of the substrates studied in the pH region (9–12.5) investigated. Higher temperature reduces the adsorbed molar amounts due to thermodynamic reasons except for benzoate which shows no change in the amounts adsorbed at different temperatures. Also, the enthalpy change resulting from adsorption of benzoate is slightly exothermic whereas the other substrates give rise to positive values, indicating endothermic adsorption processes. With respect to construction applications, the results confirm that limestone powder which is now being used as a supplemental constituent in Portland composite cements (e. g. CEM II / A-LL) has the potential to adsorb significant quantities of hetero-anionic admixtures such as polycarboxylate superplasticizers or sodium gluconate retarders.

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