

a measurement of k_G and an estimate of k_D would suffice for the calculation of k_A from eq 44.

Experimentally, estimates of b may be available from detailed studies of the variations of experimentally determined values of k_G with factors such as viscosity and temperature,¹⁰ allowing the use of eq 44 to determine k_A . Finally, picosecond kinetic methods can provide direct illumination the problem.

Asking for the value of k_A for a fast bimolecular reaction in solution might not be a very meaningful question. This constant is defined in theory as the rate constant for the reaction at equilibrium, but it is not accessible directly in experiments, at least not easily. Even if the forward and backward rates could be measured at equilibrium, some decision would have to be made as to exactly what constitutes reaction. Different types of experiments might have the effect of defining reaction differently. Thus, the value of k_A might depend on the nature of experiment or on a somewhat arbitrary decision concerning the analysis of

data. In this sense, k_A could be an illusion.

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Note Added in Proof. There now appears to be agreement on diffusion effects on fast bimolecular reactions in the presence of the backward reactions. In addition to the present work and refs 5a-d, see: (a) Burlatskii, S. F.; Ovchinnikov, A. A.; Oshanin, G. S. *Sov. Phys. JETP* 1989, 68, 1153. (b) Burlatskii, S. F.; Oshanin, G. S.; Ovchinnikov, A. A. *Phys. Chem.* 1991, 152, 13. (c) Keizer, J.; Molski, A. *Trends in Chemical Physics*, in press. (d) Molski, A.; Keizer, J. *J. Chem. Phys.*, in press.

The Hydrosodalite System $\text{Na}_{6+x}[\text{SiAlO}_4]_6(\text{OH})_x \cdot n\text{H}_2\text{O}$: Formation, Phase Composition, and De- and Rehydration Studied by ^1H , ^{23}Na , and ^{29}Si MAS-NMR Spectroscopy in Tandem with Thermal Analysis, X-ray Diffraction, and IR Spectroscopy

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Abstract: Hydrosodalites of general composition $\text{Na}_{6+x}(\text{SiAlO}_4)_6(\text{OH})_x \cdot n\text{H}_2\text{O}$ have been prepared from kaolinite and aqueous NaOH solution by hydrothermal synthesis under various conditions and subsequent NaOH extraction with water and/or thermal dehydration. Detailed characterization of the products by ^{29}Si , ^{23}Na , and ^1H MAS-NMR spectroscopy in combination with thermal analysis, powder X-ray diffraction, and infrared spectroscopy verifies the composition of the following five distinct hydrosodalite phases: $\text{Na}_8[\text{SiAlO}_4]_6(\text{OH})_2 \cdot 2\text{H}_2\text{O}$, $\text{Na}_8[\text{SiAlO}_4]_6(\text{OH})_2$ ("basic hydrosodalites"), $\text{Na}_6[\text{SiAlO}_4]_6 \cdot 8\text{H}_2\text{O}$, $\text{Na}_6[\text{AlSiO}_4]_6 \cdot 4\text{H}_2\text{O}$, and $\text{Na}_6[\text{SiAlO}_4]_6\text{H}$ ("nonbasic hydrosodalites"). Hydrosodalite phases of other compositions such as "superbasic sodalites" $\text{Na}_{10}[\text{SiAlO}_4]_6(\text{OH})_4$ and basic sodalite hydrates $\text{Na}_8[\text{SiAlO}_4]_6(\text{OH})_2 \cdot n\text{H}_2\text{O}$ with $n > 2$ proposed by several authors could not be identified. The primary product of hydrothermal synthesis is always the basic hydrosodalite $\text{Na}_8[\text{SiAlO}_4]_6(\text{OH})_2 \cdot 2\text{H}_2\text{O}$. However, the latter is partially transformed into nonbasic $\text{Na}_6[\text{SiAlO}_4]_6 \cdot 8\text{H}_2\text{O}$ sodalite due to intracage NaOH/ H_2O exchange during the washing of the crude product with water, generally applied to remove NaOH impurities from the outer surface of the crystallites. The extent of the exchange depends on the washing conditions and is very effective for microcrystalline powders but strongly reduced for large single crystals of 0.5–1 mm in size. Thus the basic hydrosodalites of composition $\text{Na}_8[\text{SiAlO}_4]_6(\text{OH})_2 \cdot n\text{H}_2\text{O}$ with $n > 2$ described previously are in fact mixtures of basic and nonbasic hydrosodalites. In contrast to the highly hydrophilic anhydrous nonbasic sodalite $\text{Na}_6[\text{SiAlO}_4]_6$, the dehydrated basic sodalite $\text{Na}_8[\text{SiAlO}_4]_6(\text{OH})_2$ is hydrophobic and cannot be rehydrated. During slow rehydration of the former an intermediate phase of composition $\text{Na}_6[\text{SiAlO}_4]_6 \cdot 4\text{H}_2\text{O}$ has been positively identified. This study clearly demonstrates the power of combined application of multinuclear MAS-NMR spectroscopy, X-ray diffraction, IR spectroscopy, and thermal analysis for providing detailed information on the specific cage fillings and host/guest chemistry in sodalites.

Introduction

The framework of 1:1 aluminosilicate sodalites consists of a perfectly periodic array of all-space filling $[4^6 6^8]$ polyhedra (" β -cages") formed by a network of alternating and corner-sharing SiO_4 and AlO_4 tetrahedra with a unit cell content of $[\text{SiAlO}_4]_6^{6-}$ (two β -cages).¹ Besides the cations M^+ compensating the negative charge of the framework, the β -cages may contain a large variety of encapsulated salt M^+A^- , hydroxide M^+OH^- , and/or water molecules. The general unit cell composition of aluminosilicate sodalites can be given by $\text{M}_{6+x}[\text{SiAlO}_4]_6\text{A}_x \cdot n\text{H}_2\text{O}$ where M and A are single-charged cations and anions, respectively. Sodalites

have attracted considerable attention because of their structural relationship with the well-known A- and X, Y-type zeolites, their cathodochromic, photochromic, and ion-conducting properties, and, more recently, their application as matrices for semiconductor superstructures in the quantum size regime (nanocomposites).² A large number of different sodalites has been synthesized, and their composition and structure have been characterized by chemical and thermal analysis, X-ray and neutron diffraction, and spectroscopic methods. Nevertheless there are still open questions concerning, e.g., the optimum synthesis conditions and procedures

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(1) Pauling, L. Z. *Kristallogr.* 1930, 74, 213.

(2) Ozlin, G. A.; Kuperman, A.; Stein, A. *Angew. Chem.* 1989, 101, 373.

for the formation of a certain sodalite composition, the phase purity and water content of the synthesized products, the detailed structure of the nonframework constituents within the sodalite cages and their interactions with the framework, the distribution of different cage fillings over the whole structure ("solid solution" or "domains" of distinctly filled β -cages), the transformation of the guest species in the β -cages by chemical and thermal treatment ("intracage chemistry"), and others. It is obvious that clear answers to those questions are essential for the potential application of sodalites as "advanced materials", e.g., in the field of the above-mentioned nanocomposites or solid-state ion conductors.

Salt-bearing sodalites can be readily prepared by hydrothermal synthesis from kaolinite, sodium hydroxide, water, and the corresponding salt as already shown in 1892 by Thugutt³ and by the later work of Barrer et al.^{4,5} If no salt is added to the reaction mixture, hydrosodalites of the general composition $\text{Na}_{6+x}[\text{SiAlO}_4]_6(\text{OH})_x \cdot n\text{H}_2\text{O}$ are formed which contain only Na^+ , OH^- , and H_2O in the β -cages.⁴ (We note in passing that the latter cage fillings may also be present in the salt-bearing sodalites due to incomplete salt entrainment in the cages during synthesis and are probably the main reason for the different water contents observed for various salt containing sodalites.) Hydrosodalites of different compositions have been reported in the literature which may be divided into the "basic" hydrosodalites $\text{Na}_8[\text{SiAlO}_4]_6(\text{OH})_2 \cdot n\text{H}_2\text{O}$ and the "nonbasic" variants $\text{Na}_6[\text{SiAlO}_4]_6 \cdot n\text{H}_2\text{O}$.⁶ In the following, the hydrosodalite composition will be specified by the numbers of $\text{Na}^+:\text{OH}^-:\text{H}_2\text{O}$ per unit cell, i.e., "8:2:n" means a basic hydrosodalite with 8Na^+ , 2OH^- , and $n\text{H}_2\text{O}$ per unit cell (i.e., 4Na^+ , 1OH^- , and $n/2\text{H}_2\text{O}$ in the β -cage) and "6:0:n" a nonbasic sodalite with 6Na^+ , no OH^- , and $n\text{H}_2\text{O}$ per unit cell (i.e., 3Na^+ , no OH^- , and $n/2\text{H}_2\text{O}$ per β -cage).⁶

There is, however, some confusion in the literature about the true cage contents of the distinct phases of hydrosodalites. From general considerations of the cage fillings, Barrer and Cole⁵ concluded that, in addition to the 3Na^+ cations compensating the charge of the aluminosilicate framework, a β -cage is able to contain either 2NaOH , or 1NaOH and $0, 1$, or $2\text{H}_2\text{O}$, or 0NaOH and $0, 1, 2, 3$, or $4\text{H}_2\text{O}$ which correspond to the compositions $10:4:0$, $8:2:n$ ($n = 0, 2, 4$), and $6:0:n$ ($n = 0, 2, 4, 6, 8$). Although the formation of a "sodium-rich hydroxysodalite" of composition $5\text{Na}_2\text{O} \cdot 3\text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot n\text{H}_2\text{O}$ from a solid-state reaction between kaolinite and sodium hydroxide has been postulated by Borchert and Keidel,⁷ the existence of the superbasic $10:4:0$ sodalite has never been proved so far. In the early work of Barrer and Falconer⁸ the composition of basic sodalite is given corresponding to $7:1:4.5$. Several compositions of basic $8:2:n$ sodalites have been reported in the literature with $1.7 \leq n \leq 6$ for the hydrated and $n = 0$ for the dehydrated forms. From X-ray diffraction of a hydrated hydroxysodalite single crystal an ideal composition of $8:2:2$ has been found by Hassan and Grundy,⁹ but the existence of a compositional range of $8:2:2$ to $8:2:4$ is expected by these authors. However, a composition of $8:2:1.7$ is given by Emiraliiev and Yamzin¹⁰ for a single crystal studied by neutron diffraction. Using wide line ^1H NMR spectroscopy, Galitskii et al.¹¹ suggested hydrosodalite compositions of $8:2:4.6$ and $8:2:6$, in agreement with Bondareva and Malinovskii¹² who concluded from geometrical considerations that the unit cell of hydrosodalite can contain two OH groups and up to six H_2O molecules. Felsche and Luger^{13,6} reported the synthesis of $8:2:n$ sodalites with $3 \leq n \leq 4$ from

kaolinite and NaOH under mild hydrothermal conditions, with decreasing water content n at increasing reaction time.¹⁴ The nonbasic $6:0:8$ sodalite has been obtained by hydrothermal extraction of NaOH from the $8:2:n$ products.^{4,6} The dehydrated $8:2:0$ and $6:0:0$ compositions have been prepared by thermal treatment of the corresponding hydrated $8:2:n$ and $6:0:8$ sodalites. The zeolitic behavior of fully reversible de- and rehydration of the $6:0:8$ sodalite has first been observed by Zhdanov et al.¹⁵ Thermoanalytical studies of the dehydration of $6:0:8$ indicated the existence of at least one intermediate phase of composition $6:0:4$.⁶ Hydrosodalites of type $6:0:n$ with $n = 0.8, 2, 4, 6$, and 8 were studied by wide line ^1H NMR; however, a binomial distribution of the number of water molecules in the β -cages has been assumed in that study.¹⁶ The crystal structures of the $8:2:2$,^{9,12} $8:2:0$,¹⁷ $6:0:8$,^{18,19} and $6:0:0$ ¹⁸ sodalites have been reported. Quasielastic neutron scattering has been applied to the $8:2:0$ phase to study the proton dynamics at temperatures between 6 and 600 K .²⁰

In this paper we reexamine the phase compositions of the hydrosodalites obtained under different synthesis conditions and show that some of the basic hydrosodalite phases reported in the literature are in fact mixtures of basic and nonbasic hydrosodalites. In addition we study the de- and rehydration behavior of the hydrosodalites and demonstrate that, in contrast to the $6:0:0$ sodalite, pure $8:2:0$ sodalite cannot be rehydrated. These and other new information on the hydrosodalite system have been obtained by means of ^{29}Si , ^{23}Na , and ^1H MAS-NMR spectroscopy in combination with thermal analysis, powder X-ray diffraction, and infrared spectroscopy. Application of multinuclear MAS-NMR has been proved to be particularly useful in these studies since it provides distinct information on the sodalite framework (^{29}Si MAS-NMR)²¹ and on the guest species in the β -cages (^{23}Na , ^1H MAS-NMR).²² Moreover, MAS-NMR can successfully be applied to powder samples of small particle sizes ($<0.1\ \mu\text{m}$) or amorphous materials which suffer from the lack of significant X-ray diffraction data. ^{29}Si chemical shifts depend sensitively on the SiOAl bond angle of the sodalite framework and consequently on the cubic unit cell constant a_0 which in turn are affected by the guest species in the β -cages.²³ ^{29}Si MAS-NMR gives, therefore, information on the type and distribution of β -cages with different cage fillings in the sodalite structure, even in short-range ordered or amorphous materials. Single narrow lines with characteristic chemical shifts are observed for pure cubic sodalite phases, while line broadenings or splittings may appear in the ^{29}Si NMR spectra for mixed compositions and/or deviations from cubic symmetry. However, the shift differences of sodalite phases of similar composition may be small and can often not be resolved in the spectra. On the other hand, the ^{23}Na MAS-NMR spectra are mainly determined by the nuclear quadrupole interaction which depends on the symmetry of the charge distribution around the ^{23}Na nucleus. Small changes in the local environment of the sodium cations within the β -cages of the hydrosodalites may induce strong changes in the line shape and line position of the spectra. ^{23}Na MAS-NMR may therefore be considered as a probe into the β -cage characterizing different types of guest species in the sodalite cavities. Finally, ^1H MAS-NMR monitors directly the

(14) Buhl, Ch.; Felsche, J.; Luger, S. In *Interaction of Water in Ionic and Nonionic Hydrates*; Kleeberg, H., Ed.; Springer: Berlin, 1987; p 71.

(15) Zhdanov, S. P.; Buntar, N. N.; Egorova, E. N. *Dokl. Akad. Nauk USSR* **1964**, *154*, 419.

(16) Ernst, H.; Pfeifer, H.; Zhdanov, S. P. *Zeolites* **1983**, *3*, 209. Pfeifer, H.; Oehme, W.; Fenzke, D. *Proc. 24th Congress Ampere*; Elsevier: Amsterdam, 1989; p 553.

(17) Luger, S.; Felsche, J.; Fischer, P. *Acta Crystallogr.* **1987**, *C43*, 1.

(18) Felsche, J.; Luger, S.; Baerlocher, Ch. *Zeolites* **1986**, *6*, 367.

(19) Felsche, J.; Luger, S.; Fischer, P. *Acta Crystallogr.* **1987**, *C43*, 809.

(20) Buehrer, W.; Felsche, J.; Luger, S. *J. Chem. Phys.* **1987**, *87*, 2316.

(21) Engelhardt, G.; Michel, D. *High-Resolution Solid-State NMR of Silicates and Zeolites*; Wiley: Chichester, 1987.

(22) Buhl, J.-Ch.; Engelhardt, G.; Felsche, J.; Luger, S. *Ber. Bunsenges. Phys. Chem.* **1988**, *92*, 176.

(23) (a) Engelhardt, G.; Luger, S.; Buhl, J.-Ch.; Felsche, J. *Zeolites* **1989**, *9*, 182. (b) Weller, M. T.; Wong, G. J. *J. Chem. Soc., Chem. Commun.* **1988**, 1103. (c) Jacobsen, H. S.; Norby, P.; Bildsoe, H.; Jacobsen, H. J. *Zeolites* **1989**, *9*, 491.

(3) Thugutt, St. J. Z. *Anorg. Allg. Chem.* **1892**, *2*, 65.

(4) Barrer, R. M.; Cole, J. F.; Sticher, H. J. *Chem. Soc. A* **1968**, 2475.

(5) Barrer, R. M.; Cole, J. F. *J. Chem. Soc. A* **1970**, 1516.

(6) Felsche, J.; Luger, S. *Thermochim. Acta* **1987**, *118*, 35.

(7) Borchert, W.; Keidel, J. *Heidelb. Beitr. Miner. Petr.* **1947**, *1*, 2.

(8) Barrer, R. M.; Falconer, J. D. *Proc. Roy. Soc.* **1956**, *A236*, 227.

(9) Hassan, I.; Grundy, H. D. *Acta Crystallogr.* **1983**, *C39*, 3.

(10) Emiraliiev, A.; Yamzin, I. I. *Sov. Phys. Crystallogr.* **1978**, *23*, 27.

(11) Galitskii, V. Yu.; Grechushnikov, B. N.; Ilyukhin, V. V.; Belov, N. V. *Sov. Phys. Dokl.* **1974**, *19*, 111. Galitskii, V. Yu.; Shcherbakov, V. N.; Gabuda, S. P. *Sov. Phys. Crystallogr.* **1973**, *17*, 691.

(12) Bondareva, O. S.; Malinovskii, Yu. A. *Sov. Phys. Crystallogr.* **1983**, *28*, 273.

(13) Felsche, J.; Luger, S. *Ber. Bunsenges. Phys. Chem.* **1986**, *90*, 731.

different kinds of water and hydroxyl protons present in the β -cages of the hydrosodalites.

Experimental Section

Preparation of Hydrosodalites. The hydrosodalite samples were prepared from kaolinite and aqueous NaOH solution using different conditions of hydrothermal synthesis (routes A–C below) or by solid-state reaction of kaolinite and NaOH (route D). Since it turned out from the very first experiments that the washing process applied to remove excess NaOH from the primary synthesis products may affect the phase composition of the final samples, a standard procedure of washing the filtered solid products four times with 25 mL of H₂O and subsequent drying at 353 K for 12 h was chosen and equally applied to all the synthesized samples described in this paper.

Route A. Crystals of pure 8:2:2 sodalite (crystal size up to 1 mm) were synthesized by hydrothermal reaction of 0.2 g of kaolinite sintered at 1723 K with 2 mL of carbonate-free 16 M aqueous NaOH solution at 623 K and 110 MPa and 7 days of reaction time in silver tubes of 8-mm diameter and 100-mm length packed in high-pressure steel autoclaves. The crystals were separated from the reaction mixture and washed and dried as given above. Thermal treatment of the crystals at 873 K for 3 h in vacuum yields the 8:2:0 sodalite. Soxhlet extraction of the 8:2:2 crystals with water at 373 K for 120 h yield the hydrous nonbasic 6:0:8 sodalite which is dehydrated to the anhydrous 6:0:0 composition by thermal treatment at 673 K for 3 h in vacuum.

Route B. Microcrystalline powders (particle size 0.5–10 μ m) of basic hydrosodalites with different water contents were obtained following Luger and Felsche⁶ from a mixture of 1 g of kaolinite and 8 mL of carbonate-free 16 M aqueous NaOH solution in 10 mL of Teflon-coated steel autoclaves at 410 K and autogeneous pressure of about 20 MPa. To study the effect of duration of synthesis on the water content of the final products,¹⁴ reaction periods of 1 h (sample B1), 1 day (B2), 7 days (B3), 14 days (B4), 25 days (B5), and 60 days (B6) were used in these experiments. The solid products were filtered and treated by the standard procedure. As described for route A, these products were transformed into the 8:2:0, 6:0:8, and 6:0:0 sodalites by thermal treatment and Soxhlet extraction.

Route C. Microcrystalline powders of basic hydrosodalites were also obtained according to Barrer et al.⁴ by heating a mixture of 2 g of kaolinite and 200 mL of 4 M aqueous NaOH at 353 K for 5 days at normal pressure under air or N₂ in a 500-mL glass flask equipped with a reflux condenser. The resulting solid product was treated as in route B.

Route D. In order to reexamine the formation of nonbasic and superbasic hydrosodalites according to Borchert and Keidel⁷ finely powdered mixtures of kaolinite and NaOH in the mole ratio of 1:2, 3:8, and 3:10 were heated at 383 K for 24 h under open conditions. The solid material was powdered and treated as described above.

Methods of Characterization. NMR Spectroscopy. ²⁹Si and ²³Na MAS NMR spectra were obtained at 79.49 and 105.84 MHz, respectively, on a Bruker MSL-400 spectrometer equipped with a double-bearing multinuclear MAS probe for 7-mm rotors. ¹H MAS-NMR spectra were measured at 500.13 MHz on a Bruker MSL-500 spectrometer using high speed MAS with 4-mm rotors. Single pulse excitation has been applied for the ¹H, ²⁹Si, and ²³Na MAS-NMR spectra, for the latter two nuclei in combination with high-power proton decoupling. ²⁹Si CP-MAS and ²³Na CP-MAS spectra were also measured for selected samples. The following conditions were used in the measurements: ²⁹Si, pulse repetition 5 s, pulse width 2 μ s, mixing time for CP 2 ms, spinning speed 4 kHz, standard tetramethylsilane; ²³Na, pulse repetition 5 s, pulse width 1 μ s, mixing time for CP 1 ms, spinning speed 4.5–5.5 kHz, standard solid NaCl; ¹H, pulse repetition 120 s, pulse width 2 μ s, spinning speed 9.5–11.3 kHz, standard tetramethylsilane.

Thermal Analysis. Thermogravimetry (TG), derivative thermogravimetry (DTG), and difference thermoanalysis (DTA) were performed simultaneously on a Netzsch Thermoanalyzer STA 429 (N₂ atmosphere, heating rate 10 K/min, Pt crucible, thermocouple Pt10%Rh/Pt).

X-ray Powder Diffraction. XRD powder photographs were obtained by the Guinier technique on a Guinier-Huber camera system 600 (Cu K α radiation, internal Si standard). The unit cell parameters were obtained by LSQS refinement (program Idex/Latcon). Densitometer traces of the photographs were registered by a Joyce Loebel Microdensitometer 3CS.

Infrared Spectroscopy. Mid-IR spectra were measured from KBr pellets of the samples using a Mattson-Polaris FT-IR spectrometer.

Results

In this section the detailed characterization of the various hydrosodalite samples by X-ray powder diffraction, thermal analysis, IR spectroscopy, and MAS-NMR spectroscopy will be

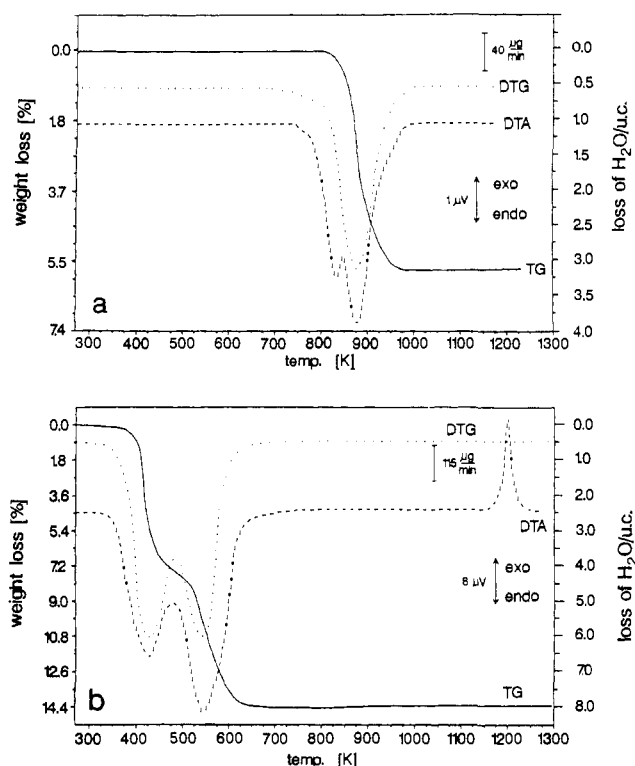


Figure 1. Simultaneous thermal analysis (TG/DTG/DTA) of hydrosodalites Na_{6+x}[SiAlO₄]₆(OH)_xnH₂O prepared by route A: (a) $x = 2$, $n = 2$ (8:2:2), sample weight 20.5 mg and (b) $x = 0$, $n = 8$ (6:0:8), sample weight 70.0 mg.

presented. Since it turned out that the 8:2:2 sodalite crystals obtained by route A and the 8:2:0, 6:0:8, and 6:0:0 sodalite phases prepared from this sample have the purest phase compositions, these products will be considered first. The results obtained from the pure phases will then be used to characterize the less well-defined microcrystalline powders prepared according to routes B–D and the rehydration products of the dehydrated 8:2:0 and 6:0:0 sodalites.

1. Basic 8:2:2 Sodalite Single Crystals Prepared by Route A. The crystal structure of the basic 8:2:2 sodalite has been determined from X-ray diffraction data by Hassan and Grundy⁹ and very recently by Wiebcke et al.²⁴ from X-ray and neutron diffraction data using materials from this work. The cubic structure has the space group $P\bar{4}3n$ with a lattice constant a_0 of 8.890 (1) Å at 295 K.⁹ The recent structure analysis of Wiebcke et al.²⁴ revealed that H₂O and OH⁻ in the β -cage form a orientationally disordered hydrogen dihydroxide anion [H–O···H···O–H]⁻ with a very strong central O···H···O hydrogen bond. Thus the constitution of the 8:2:2 sodalite is properly described by the formula [Na₄(O₂H₃)₂][SiAlO₄]₆.

The powder XRD diagram of the 8:2:2 sodalite crystals prepared according to route A shows sharp lines which all fit the cubic symmetry (space group $P\bar{4}3n$) with a lattice constant $a_0 = 8.890$ (3) Å. Thermal analysis (Figure 1a) reveals that the 8:2:2 sodalite is exceptionally stable against thermal treatment. In the temperature range of 823 to 873 K two water molecules per unit cell leave the structure to form the 8:2:0 sodalite. From 873 to 900 K another water molecule resulting from the remaining OH groups is released, while the sodalite framework is destroyed and a carnegieite-type phase Na₂O·6NaAlSiO₄ with interstitial Na₂O is formed.⁶ Therefore, the total water content obtained by thermal analysis is 3H₂O molecules per unit cell in full agreement with the ideal 8:2:2 composition.

The IR spectrum of the 8:2:2 sodalite (Figure 2a) shows a sharp OH stretching mode at 3640 cm⁻¹ originating from the terminal

(24) Wiebcke, M.; Engelhardt, G.; Felsche, J.; Kempa, P.-B.; Sieger, P.; Schefer, J.; Fischer, P. *J. Phys. Chem.*, in press.

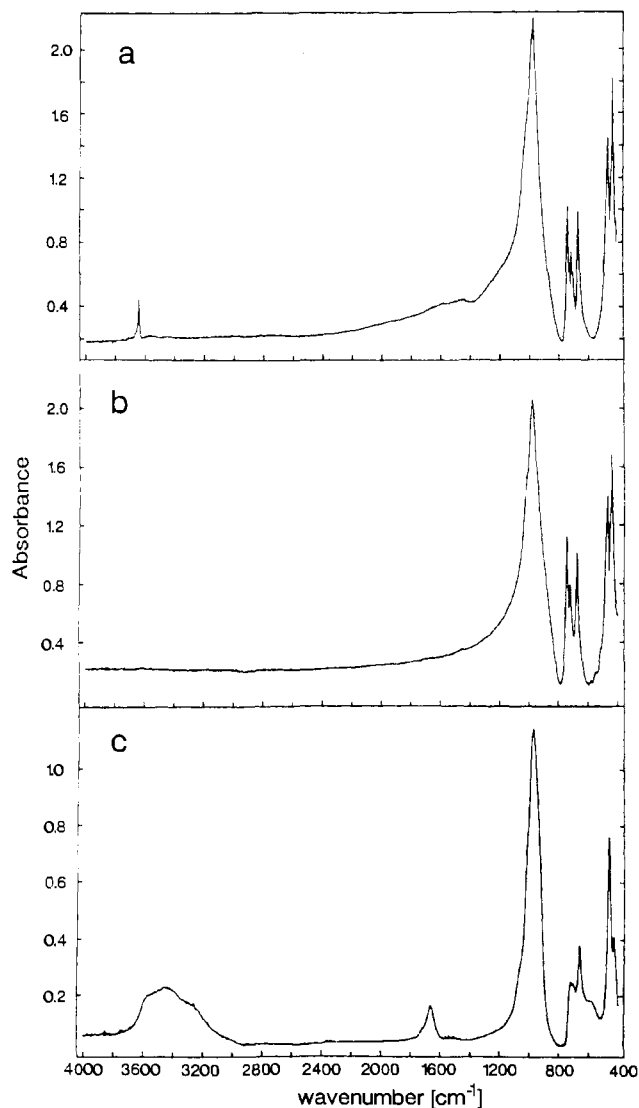


Figure 2. IR spectra of hydrosodalites of $\text{Na}_{6+x}[\text{SiAlO}_4]_6(\text{OH})_x \cdot n\text{H}_2\text{O}$ prepared by route A: (a) $x = 2, n = 2$ (8:2:2), (b) $x = 2, n = 0$ (8:2:0), and (c) $x = 0, n = 8$ (6:0:8).

OH groups of the $[\text{H}-\text{O}\cdots\text{H}\cdots\text{O}-\text{H}]^-$ anion. Due to strong hydrogen bonding the central $\text{O}\cdots\text{H}$ stretching vibration is expected to be broad and shifted strongly to lower wavenumbers.²⁵ Therefore, this vibration may tentatively be assigned to the broad absorption centered at about 1400 cm^{-1} which overlaps partly with the SiOAl stretching modes of the framework below 1200 cm^{-1} . Interestingly, no water deformation mode appears in the spectrum at about 1660 cm^{-1} , in agreement with the structure of the $[\text{H}-\text{O}\cdots\text{H}\cdots\text{O}-\text{H}]^-$ complex in the β -cage. The IR spectrum of Figure 2a differs significantly from that published recently for a hydrated hydroxysodalite by Godber and Ozin²⁶ which exhibits a broad OH stretching absorption between 3000 and 3700 cm^{-1} and a sharp water deformational mode at 1665 cm^{-1} . However, this spectrum resembles that of the nonbasic 6:0:8 sodalite shown in Figure 2c (see below).

In the ^{29}Si MAS-NMR spectrum of the 8:2:2 sodalite a single sharp line with a chemical shift of -84.3 ppm is observed which indicates a highly ordered 1:1 aluminosilicate framework.²¹ The ^1H MAS-NMR spectrum of the 8:2:2 sodalite measured at 193 K shows three sharp lines at $-0.1, 5.0,$ and 16.3 ppm accompanied by weak spinning side bands (Figure 3a). Due to their chemical shifts and integral intensity ratio of 2:1, the lines at -0.1 and 16.3 ppm have to be assigned to the terminal and central protons of

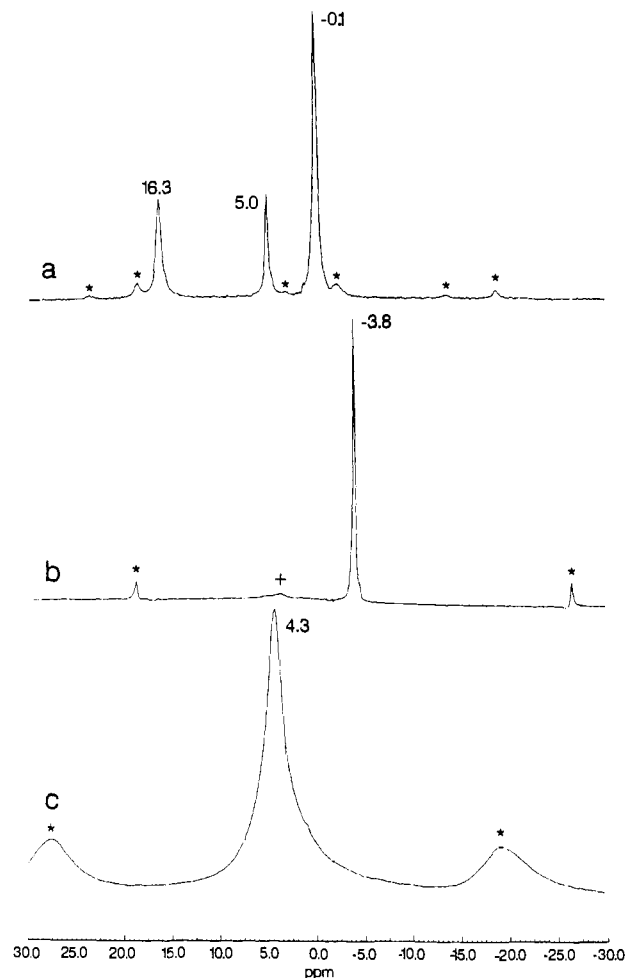


Figure 3. ^1H MAS-NMR spectra (500.13 MHz) of hydrosodalites $\text{Na}_{6+x}[\text{SiAlO}_4]_6(\text{OH})_x \cdot n\text{H}_2\text{O}$ prepared by route A: (a) $x = 2, n = 2$ (8:2:2), at 193 K, (b) $x = 2, n = 0$ (8:2:0), at 300 K, and (c) $x = 0, n = 8$ (6:0:8), at 300 K. * denotes spinning sidebands, and + denotes background signals of the probe.

the $[\text{H}-\text{O}\cdots\text{H}\cdots\text{O}-\text{H}]^-$ complex, respectively, while the line at 5.0 ppm originates from impurities (water in 6:0: n sodalite or adsorbed on residual surface NaOH). The strong low-field shift of the line of the central protons is typical of protons involved in strong hydrogen bonds,²⁷ and the shift value of 16.3 ppm is in excellent agreement with the result of an ab initio calculation of the isolated $[\text{H}_3\text{O}_2]^-$ cluster.²⁸ A chemical shift of 0.2 ppm has been calculated for the OH protons in a free water molecule not involved in any hydrogen bond.²⁸ This shift value may be compared with the shift of -0.1 ppm measured for the terminal OH groups of the $[\text{H}_3\text{O}_2]^-$ complex in the β -cages of the 8:2:2 sodalite. At room temperature and between 170 and 135 K considerable line broadening has been observed, indicating complex dynamic processes of the $[\text{H}_3\text{O}_2]^-$ guest species within the sodalite cavities. Detailed studies of these phenomena including NMR, IR, and quasielastic neutron scattering are in progress and will be reported elsewhere.

The ^{23}Na MAS-NMR spectrum of the 8:2:2 sodalite measured at 105.84 MHz exhibits a broad and symmetric line with a maximum at -2.5 ppm (see Figure 4a). The line width decreases in the spectrum measured at 132.29 MHz (Bruker MSL-500) and increases at 79.39 MHz (Bruker MSL-300), indicating second-order quadrupolar interaction of the ^{23}Na nuclei as a main source of the line broadening. The featureless line shape points to the presence of a distribution of chemical shifts and/or field gradients of the ^{23}Na nuclei possibly modified by dynamic processes of the guest species in the sodalite cavities.

(25) Emsley, J. *Chem. Soc. Rev.* **1980**, 9, 91.

(26) Godber, J.; Ozin, G. A. *J. Phys. Chem.* **1988**, 92, 4980.

(27) Jeffrey, G. A.; Younghee, Y. *Acta Crystallogr.* **1986**, B42, 410.

(28) McMichael Rohlfling, C.; Allen, L. C.; Ditchfield, R. *Chem. Phys. Lett.* **1982**, 86, 380.

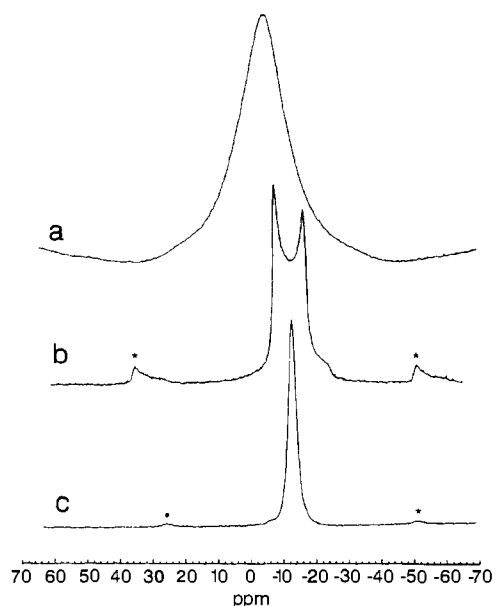


Figure 4. ^{23}Na MAS-NMR spectra (105.84 MHz) of hydrosodalites $\text{Na}_{6+x}[\text{SiAlO}_4]_6(\text{OH})_x \cdot n\text{H}_2\text{O}$ prepared by route A: (a) $x = 2, n = 2$ (8:2:2), (b) $x = 2, n = 0$ (8:2:0), and (c) $x = 0, n = 8$ (6:0:8). * denotes spinning side bands.

2. 8:2:0 Sodalite from 8:2:2 Single Crystals. The β -cage of the basic dehydrated 8:2:0 sodalite contains 4Na^+ cations and a single OH group, the oxygen atom of which is located in the center of the cage.¹⁷ The X-ray powder diffraction pattern of our sample shows slightly broadened lines and fits the cubic $P43n$ space group with $a_0 = 8.750$ (5) Å. Thermal analysis indicates that the 8:2:0 sodalite is stable up to 873 K but is decomposed at higher temperature by releasing one water molecule per unit cell and transformation into a carnegieite-type phase⁶ (see above). The IR spectrum of the 8:2:0 sodalite (Figure 2b) exhibits the characteristic pattern of the SiOAl framework vibrations below 1200 cm^{-1} , but surprisingly no OH stretching mode appears in the spectrum. Possibly the absorption of this line is too weak to be observed by the routine transmission IR technique applied. However, first results obtained by Peuker et al.²⁹ employing IR remission spectroscopy to our sample give indications of a weak OH stretching band at 3581 cm^{-1} .

The ^{29}Si MAS-NMR spectrum of the 8:2:0 sodalite consists of a sharp single line at -81.2 ppm indicating again a highly regular 1:1 aluminosilicate framework. In contrast to the hydrated 8:2:2 composition, the ^{23}Na MAS-NMR spectrum of the dehydrated 8:2:0 sodalite is characterized by a typical quadrupolar line shape with two sharp maxima at -6.4 and -17.0 ppm (Figure 4b).²² Computer simulation of the spectrum results in the quadrupole coupling constant $\text{QCC} = 2.0\text{ MHz}$, asymmetry parameter $\eta = 0.1$, and isotropic chemical shift $\delta_{\text{iso}} = -4.0\text{ ppm}$. According to this ^{23}Na NMR spectrum there is on average only one sodium environment in the β -cage, i.e., the different $\text{Na}\cdots\text{H}\cdots\text{O}$ coordinations in the cage must be averaged by dynamic exchange. This conclusion agrees with the fast rotation of the OH group in the β -cage of the 8:2:0 sodalite observed by inelastic and quasi-elastic neutron scattering.²⁰ The ^1H MAS-NMR spectrum shows a single sharp line at -3.8 ppm (Figure 3b). This exceptional high field shift of the OH proton in the 8:2:0 sodalite demonstrates the peculiar bonding character of the H atom in the matrix-isolated $[\text{Na}_4\text{OH}]^{3+}$ cluster in this structure.

3. 6:0:8 Sodalite from 8:2:2 Sodalite Single Crystals. The powder XRD pattern of the 6:0:8 sodalite prepared from 8:2:2 single crystals is typical of the cubic sodalites with $a_0 = 8.850$ (5) Å¹⁸ but shows slightly broader lines than the parent 8:2:2 sample. Thermal analysis clearly demonstrates the presence of eight water molecules per unit cell which are released between

400 and 600 K from the 6:0:8 sodalite in a two-step reaction (Figure 1b).⁶ The IR spectrum of the 6:0:8 sodalite (Figure 2c) exhibits broad bands of the H_2O stretching vibration in the range between 3000 and 3600 cm^{-1} typical of hydrate water bridged via hydrogen bonds. In addition a comparatively narrow band appears at 1660 cm^{-1} for the H_2O deformation mode. As in the other hydrosodalites below 1200 cm^{-1} the SiOAl framework vibrations are observed which, however, show some frequency shifts and intensity changes.

^{29}Si MAS-NMR of the 6:0:8 sodalite gives a narrow line at -82.5 ppm indicating that the ordered 1:1 aluminosilicate framework is retained after the hydrothermal treatment of the parent 8:2:2 composition. The ^{23}Na MAS-NMR spectrum (Figure 4c) exhibits a single, symmetrical, and narrow line at -11.0 ppm ²² which indicates dynamic exchange processes of the Na^+ cations and/or water molecules in the β -cages averaging any asymmetry and differences in the local sodium environments.^{18,19} Dynamic exchange of the water molecules¹⁶ is also responsible for the single line observed in the ^1H MAS-NMR spectrum of the 6:0:8 sodalite measured at 293 K (Figure 3c). The broadness of this line and the intense spinning side-band pattern indicate only partial dynamic averaging of the H-H dipolar coupling of the two water protons. The chemical shift of 4.3 ppm is close to the shift at normal temperature of liquid water and of water molecules in zeolites³⁰ and silica glasses.³¹

4. 6:0:0 Sodalite. Upon dehydration of the 6:0:8 sodalite to the 6:0:0 composition by thermal treatment the unit cell volume expands markedly as already shown by Felsche et al.^{13,18} The unit cell constant increases from $a_0 = 8.850$ (5) Å for the hydrated 6:0:8 to $a_0 = 9.100$ (5) Å for the dehydrated 6:0:0 sodalite. Thermal analysis (Figure 1b) reveals that the 6:0:0 sodalite is stable up to 1150 K, while at higher temperature it is transformed into carnegieite.⁶

The ^{29}Si MAS spectrum of the 6:0:0 sodalite shows a single line at -90.5 ppm which is shifted by 8.0 ppm to high field from the line of the 6:0:8 sodalite. This high field shift agrees with the increase in the unit cell constant mentioned above.^{23a} In the ^{23}Na MAS-NMR spectrum only a weak line at -13 ppm could be observed,²² which however originates most probably from small impurities of 6:0: n compositions in the 6:0:0 sample, i.e., from Na^+ cations in not fully dehydrated or partially rehydrated sodalite cavities. If all water is removed from the β -cage, the sodium cations are localized close the centers of the six-ring windows and are coordinated to six framework oxygen atoms of the same six-membered ring.¹⁸ The large field gradients at the ^{23}Na nuclei in this particular environment cause very strong quadrupole interaction and, therefore, excessive line broadening which probably makes the ^{23}Na resonance of the 6:0:0 sodalite unobservable in the normal single pulse MAS-NMR spectrum.

5. Basic Hydrosodalites Prepared by Route B. In contrast to the high-pressure, high-temperature synthesis of route A, generally microcrystalline powders of hydrosodalites with particle sizes of $0.1\text{--}10\text{ }\mu\text{m}$ are obtained at lower pressure and lower temperature applied in route B. Since low-pressure and normal-pressure syntheses (see route C below) are frequently used in the literature to prepare hydrosodalites and salt-filled sodalites of different compositions, a careful characterization of their products is of particular interest. Therefore, a series of hydrosodalite products prepared according to route B with synthesis times between 1 h and 60 days has been studied (samples B1–B6, see Experimental Section). All the primary synthesis products were treated according to the standard procedure, i.e., filtered, washed four times with 25 mL of water, and dried at 353 K for 12 h.

The scanning electron micrographs shown in Figure 5 reveal that irregular-shaped aggregates of small hydrosodalite crystallites about $0.5\text{ }\mu\text{m}$ in size are obtained during a reaction period of 1 h (sample B1, Figure 5a), while well-developed polyhedral crystals with diameters of $5\text{--}10\text{ }\mu\text{m}$ are formed during a reaction period of 60 days (sample B6, Figure 5b). Thermal analyses of samples

(29) Peuker, Ch.; Löffler, E.; Pilz, W., private communication.

(30) Pfeifer, H.; Freude, D.; Hunger, M. *Zeolites* **1985**, *5*, 274.

(31) Kohn, S. C.; Dupree, R.; Smith, M. E. *Nature* **1989**, *337*, 539.

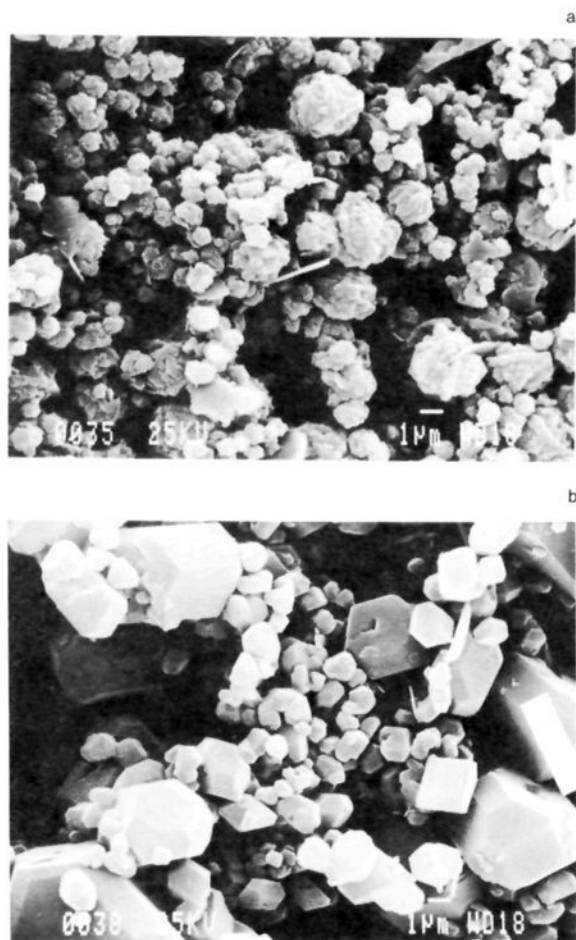


Figure 5. Scanning electron micrographs of basic hydrosodalites prepared by route B with reaction periods of (a) 1 h (sample B1) and (b) 60 days (sample B6).

B1–B6 washed according to the standard procedure show that the total water contents decrease continuously from seven H_2O molecules per unit cell for sample B1 to 3.5 $\text{H}_2\text{O}/\text{u.c.}$ for sample B6. The X-ray powder diffraction patterns of all products are typical of cubic 8:2:2 sodalite ($a_0 = 8.89 \text{ \AA}$) and differ only in the sharpness of the diffraction lines which increases with longer reaction periods due to the decrease of structural imperfections and the formation of a more regular long-range structure in the larger crystallites (see Figure 6a–d).

The ^{29}Si MAS–NMR spectra of all preparations show a single line at -84.3 ppm which, however, is markedly broadened for sample B1 but narrows for samples B2, B5, and B6 (Figure 7b–e). In contrast to ^{29}Si MAS–NMR, dramatic changes are observed in the ^{23}Na MAS–NMR spectra of the hydrosodalite powders prepared at different reaction time (Figure 8b–e). A broad and slightly asymmetric line with maximum at -11 ppm appears for sample B1, while the spectra of samples B2, B3, and B6 are characterized by a broad line at -3 ppm and a narrow line at -11 ppm . In going from sample B2 to sample B6, the -3 ppm line increases and the -11 ppm line decreases in intensity. The broad peak at -3 ppm corresponds to the spectrum measured for the 8:2:2 sodalite crystals shown in Figure 4a, while the narrow line at -11 ppm is typical of the 6:0:8 composition (Figure 4c). The ^{23}Na MAS–NMR spectra reveal, therefore, that the final products prepared by route B and subsequently washed with water and dried at 352 K consist of a mixture of basic 8:2:2 and nonbasic 6:0:8 sodalites. The proportion of the former remains larger in the samples of larger crystal size obtained by extended crystallization. However, the ^{23}Na MAS–NMR spectrum of the product synthesized with 1 h reaction time but *not washed with water* is typical of pure 8:2:2 sodalite (Figure 8a). The ^{29}Si MAS–NMR spectrum

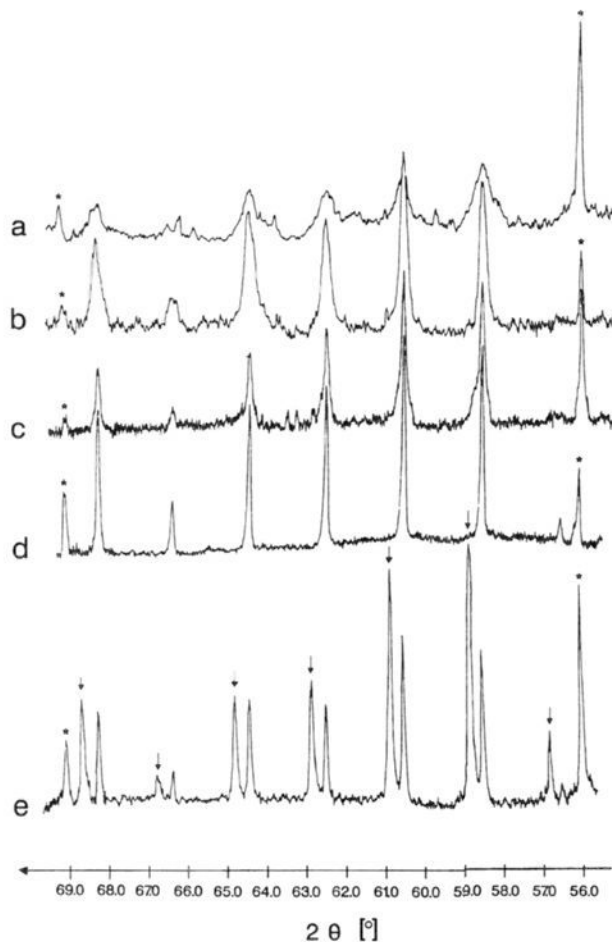


Figure 6. Powder X-ray diffraction patterns at $56^\circ \leq 2\theta \leq 69^\circ$ of basic hydrosodalites. (a–d) contain powder samples prepared by route B employing different reaction periods: (a) sample B1 (1 h), (b) sample B2 (1 day), (c) sample B5 (25 days), and (d) sample B6 (60 days). (e) 8:2:2 crystals prepared by route A after treatment with water for 3 days at 373 K . ↓ indicates the lines of the exchange product, the 6:0:8 sodalite. Lines denoted by * are from the internal Si standard.

of this sample exhibits a narrow line at -84.5 ppm (Figure 7a) in complete agreement with the pure 8:2:2 composition (see above).

6. Hydrosodalites Prepared by Route C. The microcrystalline powders obtained under normal pressure at 353 K are very similar to those prepared according to route B. Provided that CO_2 is carefully excluded from the reaction mixture, basic hydrosodalite of composition 8:2:2 is formed as initial product which again is partially transformed into 6:0:8 sodalite after washing with water. If CO_2 is present during the crystallization process, a disordered intermediate phase between cancrinite and sodalite is obtained, the powder XRD pattern of which shows diffuse reflections between sharp lines indicating strong one-dimensional disorder of AB (cancrinite) and ABC (sodalite) sequences.³² The formation of a disordered intermediate sodalite/cancrinite phase of composition $\text{Na}_{6+x}[\text{AlSiO}_4]_6(\text{CO}_3)_{x/2} \cdot n\text{H}_2\text{O}$ with $0 < x < 2$ from kaolinite, NaOH , and Na_2CO_3 by hydrothermal synthesis has also been reported by Hermeler et al.³²

7. Hydrosodalites Prepared by Route D. Powder X-ray diffraction and thermal analysis of the products obtained from solid-state reaction of kaolinite and NaOH (mole ratio 1:2, 3:8, and 3:10) according to Borchert und Keidel⁷ shows that from all compositions of the synthesis mixture only the basic 8:2:2 sodalite with $a_0 = 8.890 (5) \text{ \AA}$ is formed. Removal of excess

(32) Hermeler, G.; Buhl, J.-Ch.; Hoffmann, W. *XVth Congress of the International Union of Crystallography*, Bordeaux, 1990; Abstract C-254.

(33) Hansen, S.; Fäth, L. *Zeolites* **1982**, 2, 162.

(34) Breck, D. W. *Zeolite Molecular Sieves*; John Wiley & Sons: New York, 1974; p 636.

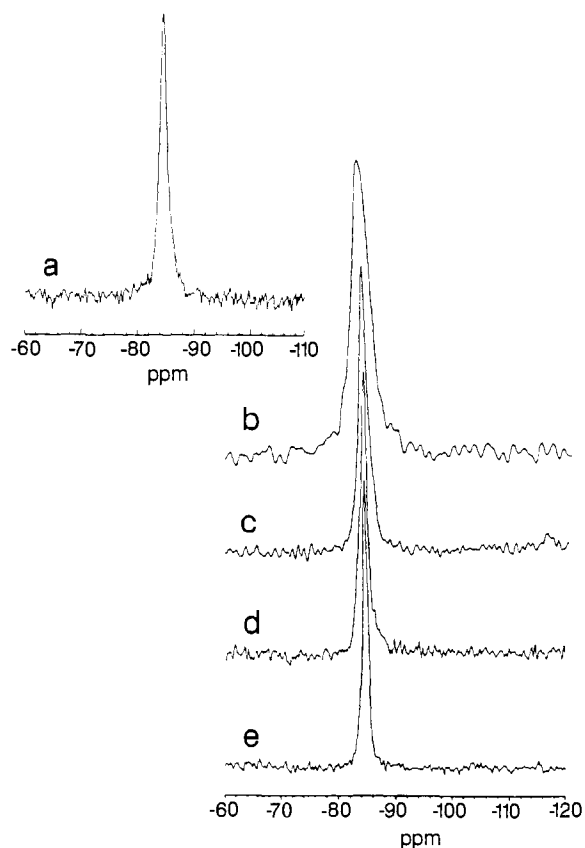


Figure 7. ^{29}Si MAS-NMR spectra (79.49 MHz) of basic hydrosodalites prepared by route B employing different reaction periods: (a) sample B1 (1 h), before washing with water. (b–e) contain water washed products: (b) sample B1 (1 h), (c) sample B2 (1 day), (d) samples B5 (25 days), and (e) sample B6 (60 days).

NaOH by washing with water leads to the formation of nonbasic 6:0:8 sodalite (see above) which, however, has not been observed as primary synthesis product. The sodium-rich "super basic" sodalite of composition 10:4: n reported by Borchert and Keidel⁷ has never been obtained in our experiments.

8. Rehydration of 6:0:0 and 8:2:0 Sodalites. Thermogravimetric, powder XRD (Figure 9a,d), and ^{29}Si MAS-NMR (Figure 10a,e) studies reveal that the anhydrous 6:0:0 sodalite can readily be rehydrated to the 6:0:8 composition. For a slurry of finely ground 6:0:0 crystals in water the rehydration is completed within 15 min, while it takes about 10 days to rehydrate a thin layer of the powdered 6:0:0 sodalite in a closed atmosphere of 65% humidity (saturator with concentrated aqueous NaNO_2 solution). The X-ray powder pattern of the same sample stored for 5 days at 65% humidity shows well-separated diffraction lines of an intermediate cubic hydrosodalite phase with a lattice constant of $a_0 = 8.965$ (5) Å accompanied by weak lines of the initial dehydrated 6:0:0 ($a_0 = 9.100$ (5) Å) and the final fully hydrated 6:0:8 ($a_0 = 8.850$ (5) Å) compositions. The changes in the X-ray diffraction diagrams with increasing time of rehydration are exemplified by the densitometer traces of the 310 and 222 reflections in Figure 9. The presence of the intermediate phase is also confirmed by the ^{29}Si MAS-NMR spectra shown in Figure 10. While the fully dehydrated 6:0:0 sodalite shows a single line at -90.5 ppm (Figure 10a), a second line at -86.5 ppm appears already after a 30-min rehydration (Figure 10b) which increases in intensity at longer rehydration times and reaches its maximum after 5 days (Figure 10d). Simultaneously the line intensity of the 6:0:8 sodalite at -90.5 ppm decreases. After complete rehydration (10 days, Figure 10e) only the line of the fully rehydrated 6:0:8 sodalite at -82.5 ppm appears in the spectrum. To discriminate the hydrated and nonhydrated sodalite phases in the spectrum more clearly, the ^{29}Si CP MAS-NMR spectra of the samples rehydrated for 3 and 5 days have also been measured and are presented in Figure 10f,g. The CP spectra show the narrow line of the partially rehydrated

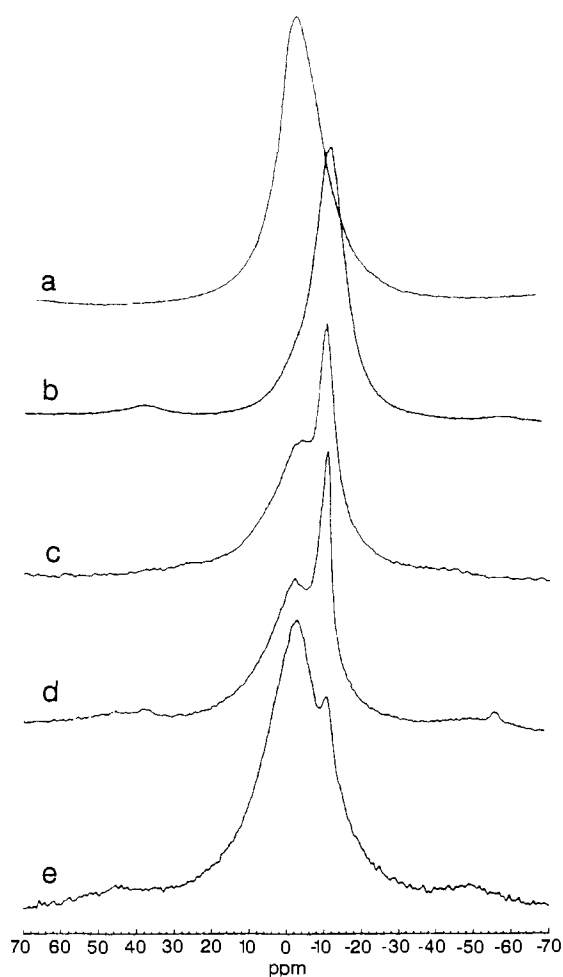


Figure 8. ^{23}Na MAS-NMR spectra (105.84 MHz) of basic hydrosodalites prepared by route B employing different reaction periods: (a) sample B1 (1 h) before washing with water. (b–e) contain water washed products: (b) sample B1 (1 h), (c) sample B2 (1 day), (d) sample B3 (7 days), and (e) sample B6 (60 days).

intermediate phase at -86.5 ppm and a weak line of the fully hydrated 6:0:8 composition, while the 6:0:0 sodalite which contains no protons for cross-polarization disappears completely from the spectrum. Thermogravimetric analysis of the sample stored for 5 days at 65% humidity results in a water content of $4\text{H}_2\text{O}/\text{u.c.}$

In contrast to the nonbasic 6:0:0 sodalite, the basic 8:2:0 sodalite cannot be rehydrated even by treatment with excess of water at higher temperature. This follows from thermogravimetric, X-ray powder diffraction, and ^{23}Na MAS-NMR studies of 8:2:0 sodalite crystals (prepared by route A) stored at 65% humidity for 10 days or slurried in water and heated at 373 K for 12 h. No changes in the water content, unit cell constant, and ^{23}Na MAS-NMR spectrum (Figure 11a) could be observed after those treatments. However, after rehydration of the "8:2:0" powder sample (prepared by dehydration of sample B6) at 65% humidity for 10 days the ^{23}Na MAS-NMR spectrum shown in Figure 11b is obtained. The spectrum exhibits the typical quadrupolar pattern of the dehydrated 8:2:0 sodalite (see Figure 4b) superimposed by a peak at -11 ppm which corresponds to the hydrated nonbasic 6:0:8 sodalite (see Figure 4c). Using ^{23}Na CP-MAS-NMR only the latter line is visible in the spectrum (Figure 11c) due to effective cross-polarization between the water protons and the ^{23}Na nuclei in the β -cage. Clearly, the 6:0:8 sodalite is formed by rehydration of the 6:0:0 impurities present in the dehydrated 8:2:0 powder sample (see section 5), while the 8:2:0 sodalite itself remains completely dehydrated.

Discussion

Formation and Phase Composition of Hydrosodalites. The aim of this study was not to reinvestigate the complete crystallization

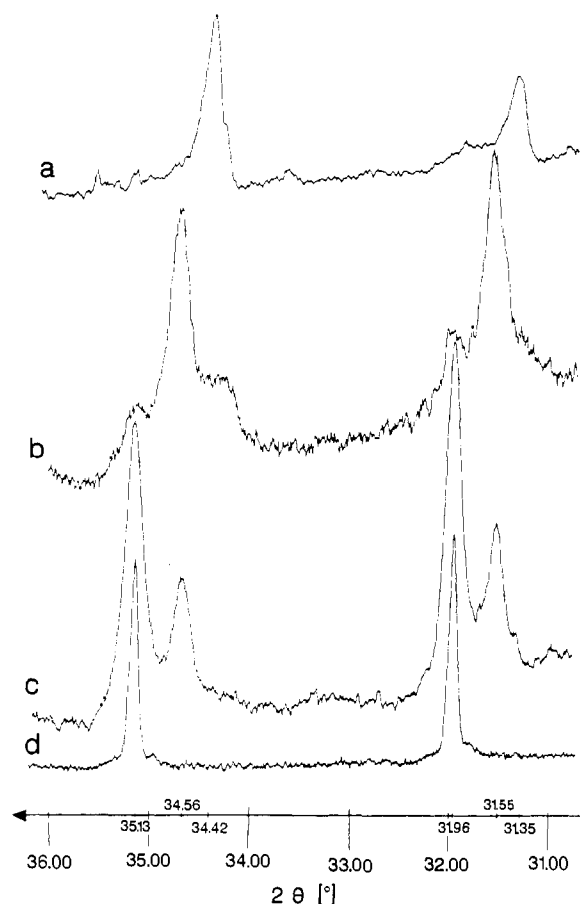
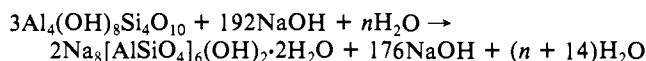
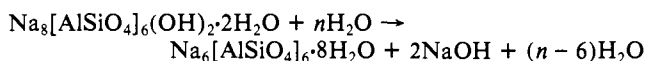


Figure 9. X-ray powder patterns at $31^\circ \leq 2\theta \leq 36^\circ$ showing the 310 (left) and 222 (right) reflections of (a) dehydrated sodalite $\text{Na}_6[\text{SiAlO}_4]_6$ (6:0:0) and the products rehydrated at 65% humidity for (b) 5 days, (c) 7 days, and (d) 10 days. Line assignments: $2\theta = 34.42^\circ$ and 31.35° , anhydrous 6:0:0 sodalite; $2\theta = 35.13^\circ$ and 31.96° , fully hydrated 6:0:8 sodalite; $2\theta = 34.56^\circ$ and 31.55° , intermediate 6:0:4 sodalite (see text).

field of hydrosodalites in the quaternary system $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ but rather to characterize the true phase compositions of the products obtained by the most common synthesis procedures and to establish reliable routes for the preparation of phase pure hydrosodalite materials. Starting from reaction mixtures of kaolinite and concentrated aqueous NaOH solutions preferably hydrothermal synthesis at different temperature and pressure has been used in the literature. The results presented above demonstrate clearly that by these procedures always the basic 8:2:2 sodalite is formed as primary synthesis product. As an example, the reaction following route B may be described by the equation



The large excess of NaOH is essential for the formation of sodalites (at lower NaOH concentrations other phases, especially nephelin hydrate I $\text{Na}_3\text{Al}_3\text{Si}_3\text{O}_{12} \cdot 2\text{H}_2\text{O}$,³³ are formed) but requires washing of the solid synthesis products with water to remove residual NaOH from the surface of the crystallites. Our results show, however, that during this washing process also intracage NaOH may be partially exchange by H_2O yielding a hydrosodalite consisting of β -cages filled with 4Na^+ , H_2O , and OH^- (corresponding the 8:2:2 composition) or 3Na^+ and $4\text{H}_2\text{O}$ (6:0:8):



The extent of this exchange depends on the amount of water used for washing and, in particular, on the specific surface of the solid synthesis products, i.e., on the size of the crystallites. While sodium hydroxide extraction from the sodalite cages is negligible for large crystals of the 8:2:2 sodalite as obtained from high-pressure/

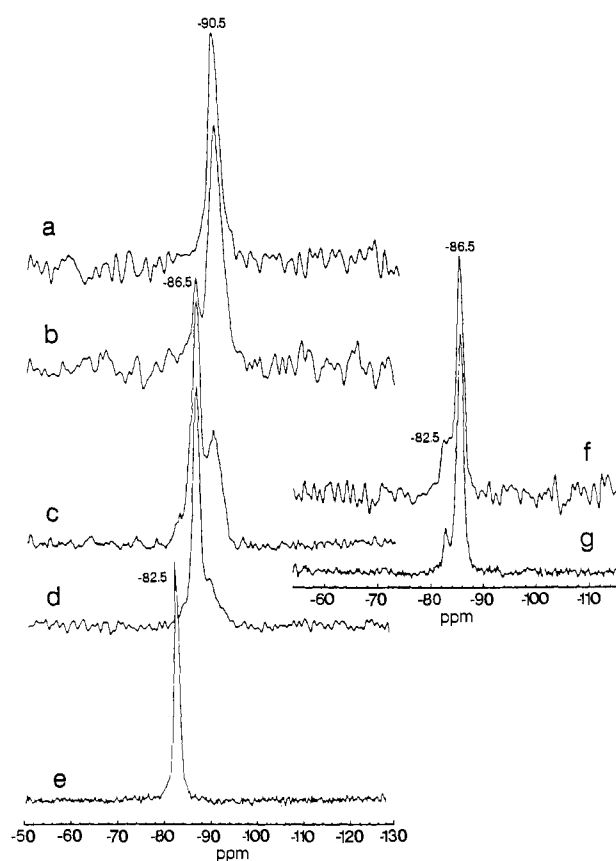


Figure 10. ^{29}Si MAS-NMR spectra (79.49 MHz) of (a) dehydrated sodalite $\text{Na}_6[\text{SiAlO}_4]_6$ (6:0:0) and the products rehydrated at 65% humidity for (b) 30 min, (c) 3 days, (d) 5 days, and (e) 10 days, (f) ^{29}Si CP-MAS NMR spectrum of (c), and (g) ^{29}Si CP-MAS NMR spectrum of (d). Line assignments: -90.5 ppm, dehydrated 6:0:0 sodalite; -82.5 ppm, fully hydrated 6:0:8 sodalite; -86.5 ppm, intermediate 6:0:4 sodalite (see text).

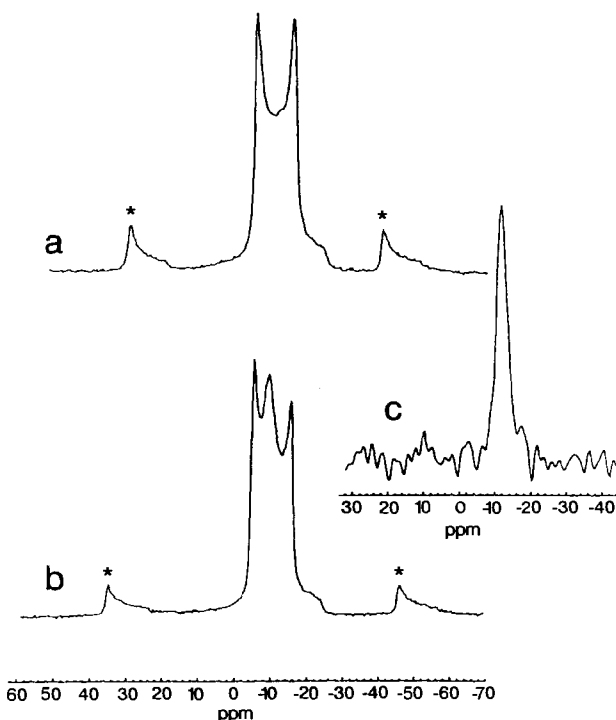


Figure 11. ^{23}Na MAS-NMR spectra (105.84 MHz) of (a) 8:2:0 sodalite crystals prepared by route A after treatment with water at 373 K for 12 h, (b) 8:2:0 sodalite powder sample prepared from sample B6 after treatment at 65% humidity for 10 days, and (c) ^{23}Na CP-MAS-NMR spectrum of (b). * denotes spinning side bands.

high-temperature synthesis (route A), it is very effective for the microcrystalline powders prepared at low or normal pressure and lower temperature (routes B and C). Moreover, at constant washing conditions the extent of intracage NaOH/H₂O exchange decreases with increasing particle size of the powder products, as shown by the decreasing water content and the ²³Na MAS-NMR spectra of Figure 8 (see section 5). Clearly, the large and irregular surface of the small hydrosodalite particles of sample B1 (see Figure 5a) is more accessible to water attack, and, therefore to intracage NaOH/H₂O exchange, than the much smaller and regular surface of the well-developed crystallites of sample B6 (see Figure 5b).

Surprisingly, the powder XRD patterns of the water-washed microcrystalline samples B1, B2, B5, and B6 shown in Figure 6a–d exhibit only the diffraction lines of the 8:2:2 composition and give no indication of the 6:0:8 sodalite phase. Supposing a phase boundary reaction of the NaOH/H₂O exchange during the washing process, the 6:0:8 composition is preferably formed at the outer layers of the crystallites. The dimensions of these layers may be too small (i.e., below the coherence length of X-ray diffraction of about 0.05 μm) to be observed by X-ray diffraction. However, the powder XRD pattern of the product obtained from large crystals of 8:2:2 sodalite by treatment with water at 373 K for three days shows well-separated reflections of the 8:2:2 and 6:0:8 sodalite phases (Figure 6e). Under these more stringent conditions a higher degree of NaOH/H₂O exchange is achieved with the formation of large-phase domains of 6:0:8 sodalite at the outer part of the crystals giving rise to pronounced X-ray diffraction lines of the 6:0:8 composition.

The conclusion is that hydrosodalite powders of composition 8:2:2 are formed as primary products from mild hydrothermal synthesis (similar to routes B or C) which, however, are partly transformed into 6:0:8 compositions due to exchange of intracage NaOH against H₂O during the subsequent washing process. Therefore, the washed products are no longer pure phases of basic 8:2:2 sodalites but always contain certain amounts of nonbasic 6:0:8 sodalites. The proportion of the latter increases with the specific surface of the polycrystalline material which is controlled by the conditions of the hydrothermal synthesis. We believe that all so called basic hydrosodalites or hydroxysodalites of type 8:2:*n* with *n* > 2 reported in the literature are in fact such mixtures of basic 8:2:2 and nonbasic 6:0:8 hydrosodalites and that pure phases of 8:2:*n* compositions with *n* > 2 do not exist. Thus the basic hydrosodalite of composition 8:2:4 described by Felsche and Luger^{13,6} (for which with respect to the rather broad powder XRD lines a lattice constant at 295 K of *a*₀ = 8.89 (1) is more realistic than the value of *a*₀ = 8.903 (1) Å given by these authors) is a phase mixture of 60% 8:2:2 and 40% 6:0:8 sodalite. The upper limit of one H₂O per β-cage of the basic hydrosodalite is also corroborated by the detailed structure analysis of the 8:2:2 sodalite indicating that the coordination of additional water molecules in the β-cage containing the [Na₄(H₃O₂)]³⁺ cluster is very unlikely.²⁴ Basic 8:2:2 sodalite crystals of high-phase purity may be obtained from high-pressure/high-temperature hydrothermal synthesis according to route A given above or of considerable purity by mild hydrothermal synthesis (route B) with long reaction periods of at least 60 days and washing the primary synthesis products with small portions of water. It is obvious that pure phases of 8:2:0 sodalites can only be obtained by thermal treatment of pure 8:2:2 samples, while pure nonbasic 6:0:8 sodalites may be prepared from any 8:2:2/6:0:8 composition by intensive NaOH extraction with hot water (see above). Thermal dehydration of the 6:0:8 products yield the anhydrous 6:0:0 sodalite.

Rehydration Behavior of 6:0:0 and 8:2:0 Sodalites. The slow rehydration (e.g., at 65% humidity, see section 8 above) of the anhydrous 6:0:0 sodalite to the fully hydrated 6:0:8 sodalite proceeds via partially rehydrated 6:0:*n* compositions with 0 < *n* < 8. If it is assumed that specific interaction energies which may lead to preferential cage fillings can be neglected, a uniform or binomial¹⁶ distribution of the water molecules among the β-cages is to be expected. In that case, with increasing degree of rehydration a steady decrease of the unit cell constant and, therefore,

continuous shifts and possibly broadenings of the X-ray diffraction lines as well as the ²⁹Si NMR peaks should be observed. However, the line splittings clearly visible in the X-ray powder patterns of Figure 9b,c and in the ²⁹Si MAS-NMR spectra of Figure 10b–d reveal the formation of a distinct partially rehydrated sodalite phase characterized by a unit cell constant of *a*₀ = 8.965 (5) Å and a ²⁹Si chemical shift of δ(Si) = –86.5 ppm. Both values are well in the middle between the corresponding data of the initial anhydrous 6:0:0 sodalite (*a*₀ = 9.100 Å, δ(Si) = 90.5 ppm) and the fully hydrated 6:0:8 sodalite (*a*₀ = 8.850 Å, δ(Si) = –82.5 ppm) indicating the formation of a 50% rehydrated sodalite phase of composition 6:0:4. After 5 days of rehydration at 65% humidity the X-ray reflections and ²⁹Si NMR lines of the intermediate phase have the highest intensity and are accompanied by only weak lines of similar intensities of the 6:0:0 and 6:0:8 sodalite (see Figures 9b and 10d). Since thermogravimetry of this sample gives a total water content of 4 molecules per unit cell, and the mean water content of the small and approximately equal proportions of 6:0:8 and 6:0:0 sodalite is also 4H₂O/u.c., a composition of 6:0:4 follows for the intermediate phase, in full agreement with the unit cell constant and ²⁹Si chemical shift considered above. Interestingly, in the course of rehydration no specific lines of other partially rehydrated 6:0:*n* phases with 0 < *n* < 4 or 4 < *n* < 8 are observed neither in the XRD patterns nor in the ²⁹Si MAS-NMR spectra. It has to be concluded, therefore, that there is a preference for the inclusion of two (6:0:4 composition) or four water molecules (6:0:8 composition) in the β-cage of the nonbasic hydrosodalites, while a uniform or binomial¹⁶ distribution of water molecules among the cages of partially rehydrated sodalite compositions seems to be less favorable. Clearly, this conclusion contradicts the above assumption about preferential cage fillings being negligible. The stability of the [Na₃(H₂O)₂]³⁺ cluster in the β-cage may be explained by specific interactions of the water molecules with the sodium cations and/or the oxygen atoms of the sodalite framework in that particular structure. Further work to prepare phase-pure samples of 6:0:4 hydrosodalite and to determine its crystal structure is in progress.

Different to the nonbasic 6:0:0 sodalite, the basic 8:2:0 sodalite is hydrophobic and cannot be rehydrated. Possibly, the openings of the six-ring windows of the β-cages in the 8:2:0 structure are too small to allow the H₂O molecules to enter the cages. In fact, the free diameter of the six rings calculated from crystal structure data^{17,18} is 2.0 Å for the 8:2:0 sodalite but 2.5 Å for the 6:0:0 sodalite which may be compared with the kinetic diameter of the water molecule of 2.65 Å.³⁴ Moreover, the β-cages of the 8:2:0 sodalite may not be accessible to H₂O molecules due to blocking of the windows by the sodium cations located near to the center of each six ring of this structure. In contrast, only six of eight six-ring windows are blocked by Na⁺ cations in the nonbasic 6:0:0 structure. The rehydration of the 8:2:0 sodalite may further be hindered by high activation energies necessary for the reconstitution of the [Na₄(H₃O₂)]³⁺ complex in the 8:2:2 phase starting from the oxygen-centered [Na₄(OH)]³⁺ complex of the 8:2:0 sodalite.

Conclusions

In brief, the main results obtained from this study are the following.

- Employing ²⁹Si, ²³Na, and ¹H MAS-NMR spectroscopy in combination with thermal analysis, powder X-ray diffraction, and infrared spectroscopy, the composition of the following five distinct hydrosodalite phases has been verified: Na₈[SiAlO₄]₆-(OH)₂·2H₂O, Na₈[SiAlO₄]₆(OH)₂, Na₆[SiAlO₄]₆·8H₂O, Na₆-[AlSiO₄]₆·4H₂O, and Na₆[SiAlO₄]₆. Considering the arrangement of the guest species in the sodalite cages we suggest to describe the above hydrosodalites more properly by the following constitution formulas: [Na₄(O₂H₃)₂][SiAlO₄]₆, [Na₄(OH)₂][SiAlO₄]₆, [Na₃□(OH)₂]₂[SiAlO₄]₆, [Na₃□(OH)₂]₂[SiAlO₄]₆, and [Na₃□]₂[SiAlO₄]₆ (where □ means an unoccupied Na⁺ position of the tetrahedral Na₄⁴⁺ arrangement in the cage). No other hydrosodalite phases of compositions such as “superbasic sodalites” [Na₅(OH)₂]₂[SiAlO₄]₆ and hydroxysodalite hydrates [Na₄-

(OH)(OH₂)_n][SiAlO₄]₆ with $n > 1$ proposed by several authors could be identified.

2. Hydrothermal reaction of kaolinite and concentrated aqueous NaOH solution under various conditions yields basic hydrosodalite [Na₄(O₂H₃)₂][SiAlO₄]₆ as the primary synthesis product. However, the latter may be partly transformed into nonbasic [Na₃□(OH₂)₄]₂[SiAlO₄]₆ sodalite due to exchange of intracage NaOH against H₂O during washing the crude product with water to remove excess NaOH from the outer surface of the crystallites. The extent of intracage NaOH/H₂O exchange depends on the washing conditions and the specific surface (crystallite size) of the synthesis products. The extraction of NaOH from the cages by H₂O washing is considerably reduced only for large single crystal products (crystal size 0.5–1 mm) prepared under high-pressure/high-temperature conditions of hydrothermal synthesis according to route A.

3. Basic hydrosodalite hydrates [Na₄(OH)(OH₂)_n][SiAlO₄]₆ with $n > 1$ frequently described in the literature do not exist but are mixtures of basic [Na₄(O₂H₃)₂][SiAlO₄]₆ and nonbasic [Na₃□(OH₂)₄]₂[SiAlO₄]₆ sodalites. These mixtures are formed by the above-mentioned intracage NaOH/H₂O exchange during

the washing process of the primary [Na₄(O₂H₃)₂][SiAlO₄]₆ synthesis product.

4. The dehydrated hydroxysodalite [Na₄(OH)]₂[SiAlO₄]₆ cannot be rehydrated to the [Na₄(O₂H₃)₂][SiAlO₄]₆ composition even in excess of water at higher temperature. In contrast, the anhydrous nonbasic sodalite [Na₃□]₂[SiAlO₄]₆ is highly hydrophilic and rehydrates with water to the [Na₃□(OH₂)₄]₂[SiAlO₄]₆ sodalite via an intermediate phase of composition [Na₃□(OH₂)₂]₂[SiAlO₄]₆.

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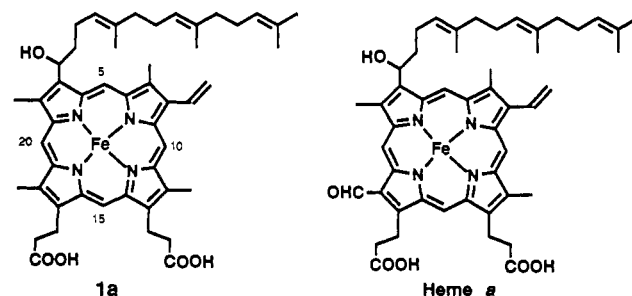
Structure of the Heme *o* Prosthetic Group from the Terminal Quinol Oxidase of *Escherichia coli*

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Abstract: The structure of the heme *o* prosthetic group of *Escherichia coli* quinol oxidase (cytochrome *o* oxidase) has been unambiguously determined by preparation and characterization of its iron-free derivative porphyrin *o* dimethyl ester, or dimethyl 2,7,12,18-tetramethyl-3-[(4*E*,8*E*)-1-hydroxy-5,9,13-trimethyltetradeca-4,8,12-trienyl]-8-vinylporphine-13,17-dipropionate. The identity of this natural porphyrin dimethyl ester was established by ¹H NMR, MS, IR, and RR spectroscopies as well as by comparisons with model compounds and the closely related porphyrin *a* dimethyl ester. The reliability of the structure determination was further strengthened by the isolation and characterization of the acetylated and dehydrated derivatives of porphyrin *o*.

Aerobically grown *Escherichia coli* express two membrane-bound, multi-heme respiratory proteins: cytochrome *o* oxidase at high O₂ concentration and cytochrome *d* oxidase at low O₂ level.^{1–4} Both are linked to hydrogenases via a ubiquinone pool. Cytochrome *d* oxidase has two b-type hemes and an oxygen-binding d-type heme which catalyzes O₂ reduction to H₂O. The structure of the heme *d* prosthetic group was recently established by spectral characterizations⁵ and by total synthesis.⁶ In contrast, cytochrome *o* oxidase has two hemes and one Cu ion⁷ where one heme and the copper center form a binuclear metal catalytic site³ for binding and reduction of O₂. Therefore, this enzyme bears a strong resemblance to mitochondrial aa₃ cytochrome oxidase, which is also exhibited by the primary protein structure.² Since the absorption spectrum of the cytochrome *o* heme group is roughly similar to b-type hemes, its structure had been assumed to be that of protoheme. Recently, Puustinen and Wikström⁸ have suggested that the hemes of cytochrome *o* are of a novel kind, for which they proposed the name heme *o*. The structure of heme *o* (**1a**) was proposed to be heme *a* like, containing a 17-carbon farnesylhydroxyethyl side chain but with a methyl residue replacing the formyl group at pyrrole ring D. This proposed



structure was based on the following observations: (1) Chromatographic analysis of the extracted heme *o* revealed that it is

- (1) Anraku, Y.; Gennis, R. B. *Trends Biochem. Sci.* **1987**, *12*, 262–266.
- (2) Chepur, V.; Lemieux, L.; Au, C. C.-T.; Gennis, R. B. *J. Biol. Chem.* **1990**, *265*, 11185–11192.
- (3) (a) Salerno, J. C.; Bolgiano, B.; Poole, R. K.; Gennis, R. B.; Ingledew, W. J. *J. Biol. Chem.* **1990**, *265*, 4364–4368. (b) Bolgiano, B.; Salmon, I.; Ingledew, W. J.; Poole, R. K. *Biochem. J.* **1991**, *274*, 723–730.
- (4) Miller, M. J.; Gennis, R. B. *J. Biol. Chem.* **1983**, *258*, 9159–9165.
- (5) (a) Tlmkovich, R.; Cork, M. S.; Gennis, R. G.; Johnson, P. Y. *J. Am. Chem. Soc.* **1985**, *107*, 6069–6075. (b) Andersson, L. A.; Sotiriou, C.; Chang, C. K.; Loehr, T. M. *J. Am. Chem. Soc.* **1987**, *109*, 258–264.
- (6) Sotiriou, C.; Chang, C. K. *J. Am. Chem. Soc.* **1988**, *110*, 2264–2270.

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