déduisant par translation. Ces mêmes valeurs sont égales (2,94 Å) dans le succinamide.

Le plan moyen des liaisons hydrogène a pour équation:

$$x - 0{,}0858y - 0{,}0480z - 3{,}5003 = 0 .$$

Le plan moyen du groupement amide calculé par une méthode de moindres carrés a pour équation:

$$x - 0{,}0778y + 0{,}0140z - 3{,}6020 = 0 .$$

Les atomes de carbone constituant la chaîne semblent rigoureusement dans le plan d'équation:

$$x + 0{,}1372y - 0{,}0232z - 3{,}8417 = 0 .$$

L'angle dièdre du plan de la chaîne de carbone et du plan du groupement amide est de 8° 30, l'arête d'intersection étant confondue avec C(3)–C(4). L'angle dièdre du plan du groupement amide et du plan des liaisons hydrogène est d'environ 3°.

Les écarts en Å des atomes d'oxygène et d'azote au plan de la chaîne sont:

$$-0{,}225 \text{ Å et } 0{,}263 \text{ Å} .$$

L'arrangement des molécules dans la maille se présente comme une succession de feuillets parallèles au plan (20$\bar{1}$) et équidistants d'environ 3,7 Å.

Les grandeurs et les cosinus directeurs des axes de l'éllipsoïde d'agitation thermique de chaque atome par rapport au système d'axes rectangulaires $x'yz$ sont donnés au Tableau 5.

La Fig. 4 représente la projection de l'éllipsoïde d'agitation thermique de chaque atome suivant [010]. La plus forte valeur du coefficient thermique est dans la direction perpendiculaire au plan de la molécule et du feuillet. Les atomes d'oxygène et d'azote des bouts de chaînes ont une agitation thermique transversale (perpendiculaire au plan) plus prononcée que les atomes de carbone de la chaîne.

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Sodium Silicate Hydrates. I. Crystallographic Data

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Crystals of the five hydrated sodium silicates obtainable at room temperature have been grown. Their unit cells and space groups were determined by X-ray single-crystal methods, and the results compared with goniometric data. X-ray powder patterns were obtained and indexed.

Introduction

Extensive studies of phase equilibria in the system Na_2O–SiO_2–H_2O (Sprauer & Pearce, 1940; Lange & Stackelberg, 1948; Baker, Jue & Wills, 1950; Baker & Jue, 1950; Wills, 1950) have established the existence of a variety of sodium silicate hydrates. Table 1 lists some of these compounds, with the results of careful goniometric studies. Other work is summarized by Vail (1952). The X-ray work reported hitherto has been limited to some powder patterns (Powder Diffraction File, cards no. 1–1107, 2–0465, 3–0432; Ryskin, Stavitskaya & Mitropolsky, 1964) and a determination of the unit cell of Na_2O . SiO_2 . $9H_2O$ (Lange & Stackelberg, 1948).

There have been speculations about the nature of the anions in these compounds. Thilo & Miedreich (1951) suggested that the anions are of the form $[H_2SiO_4]^{2-}$ or $[HSiO_4]^{3-}$ (according to the composition of the compound) basing their ideas on cryoscopic studies which are of limited relevance to the solid state. Infrared studies (Ryskin, Stavitskaya & Mitropolsky, 1964; Manvelyan, Babayan & Gazaryan, 1964) have shown the existence of Si–O–H bonding and absence of Si–O–Si bonding in at least some of the compounds. The results of extraction studies (Wiecker & Slade, 1965) are consistent with anions consisting of isolated $[H_xSiO_4]^{(4-x)-}$ groups.

Confirmation of these speculations by X-ray structural analysis has hitherto been lacking. The present

paper describes the complete X-ray characterization of the compounds, undertaken as a preliminary to the determination of their structures.

Experimental

Solutions of widely varying $Na_2O : SiO_2 : H_2O$ ratios were prepared and stored in sealed polythene bottles at room temperature. After periods of days or weeks, crystals were deposited from most of them. The crystals were dried and identified by analysis and by accurate measurement of their refractive indices.

When the preparations were begun, the solutions which should have yielded crystals of $Na_2O . SiO_2 . 9H_2O$ remained clear for many weeks. This was unexpected, as previous workers had no trouble preparing this compound. It was then realized that in previous studies $Na_2O . SiO_2 . 9H_2O$ had been prepared in *glass* containers, for use as a starting material. When an appropriate solution was transferred to a glass container, $Na_2O . SiO_2 . 9H_2O$ crystals formed without difficulty, and could then be used to seed the solutions in polythene bottles.

Only one of the many solutions prepared yielded crystals of $Na_2O . SiO_2 . 8H_2O$; this reflects its narrow range of stability at room temperature.

The dried crystals have to be handled with care, because they are liable to contamination by atmospheric moisture and carbon dioxide and some of them tend to decompose to lower hydrates. Single crystals for X-ray work can be adequately protected by a thin layer of petroleum jelly. Preparation of samples for powder studies is more difficult, because grinding increases the likelihood of both contamination and decomposition. The best results were obtained when the crystals were ground in sealed plastic vials with plastic balls, using an automatic mixer-mill.

Unit cells and space groups were determined from oscillation, rotation, Weissenberg and precession photographs. Powder data were obtained by both film and diffractometer techniques. Slow speed ($0.5°$ 2θ.min^{-1}) diffractometer traces calibrated with an internal silicon standard provided accurate d values, but intensities measured from diffractometer traces were rather unreliable and estimates were, where possible, made from film. Lines were indexed by direct comparison of rotation and powder photographs taken on the same 6 cm diameter camera. Indices assigned were checked against a list of strong reflexions compiled from Weissenberg and precession photographs. When as many lines as possible had been assigned unambiguous indices, the cell parameters were refined to give the best fit with the powder data.

For four of the hydrates, densities were available from the literature and were used to calculate Z. The density of $3Na_2O . 2SiO_2 . 11H_2O$ has not previously been determined. The crystals of this hydrate were very small and tended to carry inclusions and to decompose easily. It was thus felt that their density could not be determined accurately by conventional methods. The density was therefore calculated after the manner of Howison & Taylor (1957), who derived an empirical relation between the densities and refractive indices of the various calcium silicates based on the Lorentz–Lorenz equation:

$$R = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{D}$$

where R = molar refraction, n = mean refractive index, M = formula weight and D = density.

An expression for R can be deduced empirically using data for all the well-characterized anhydrous and hydrated sodium silicates whose refractive indices and

Table 1. *Comparison of X-ray and goniometric data*

Compound	Crystal class[1]	Space group[2]		a	b	c	α	β	γ	Source
								Axial ratios and angles		
$Na_2O . SiO_2$ 5H_2O	$\bar{1}$	$P\bar{1}$	⎧	0.698	: 1 :	0.893	51.5°	81.9°	71.1°	X-ray[3]
			⎨	0.6970	: 1 :	0.8963	51°52′	81°47′	70°10′	Goniometry (a)
			⎩	0.6958	: 1 :	0.8958	50°56′	82°2′	70°43′	Goniometry (b)
$Na_2O . SiO_2 . 6H_2O$	2	$P2_1$	⎧	1.918	: 1 :	1.064		77.9°		X-ray[4]
			⎨	1.9211	: 1 :	1.0727		77°51′		Goniometry (a)
			⎩	1.9095	: 1 :	1.0720		77°53′		Goniometry (b)
$Na_2O . SiO_2 . 8H_2O$	$2/m$	$P2_1/c$	⎧	0.662	: 1 :	0.707		65.2°		X-ray[5]
			⎩	0.6644	: 1 :	0.7148		65°23′		Goniometry (b)
$Na_2O . SiO_2 . 9H_2O$	mmm	$Ibca$	⎧	0.689	: 1 :	0.681				X-ray[6]
			⎨	0.6919	: 1 :	0.6848				Goniometry (a)
			⎩	0.6830	: 1 :	0.6754				Goniometry (b)
$3Na_2O . 2SiO_2 . 11H_2O$		$Pbca$	⎧	0.925	: 1 :	1.100				X-ray[7]
			⎩	0.884	: 1 :	1.10				Goniometry (c)

(1) From goniometry.
(2) From systematic absences, combined with goniometric data where necessary.
(3) X-ray cell transformed to goniometric axes by the matrix [$\bar{1}$00/011/001].
(4) Taking β acute to conform with the goniometric data.
(5) Transformed by matrix [001/010/101].
(6) With c doubled.
(7) With a and c interchanged.

(a) Baker, Woodward & Pabst (1933).
(b) Lange & Stackelberg (1948).
(c) Morey (1934).

Table 2. *Unit-cell parameters for some sodium silicate hydrates, refined from powder data*

	a (Å)	b (Å)	c (Å)	α	β	γ	Space group	V (Å³)	Z	Density Obs. g.cm⁻³	Calc. g.cm⁻³
Na₂O . SiO₂ . 5H₂O	6·68	7·93	8·55	109·1°	98·1°	105·0°	$P\bar{1}$	401	2	1·75[1]	1·75
Na₂O . SiO₂ . 6H₂O	11·43	5·96	6·34		102·1		$P2_1$	422	2	1·81[1]	1·81
Na₂O . SiO₂ . 8H₂O	8·96	13·54	9·99		119·6		$P2_1/c$	1053	4	1·67[1]	1·67
Na₂O . SiO₂ . 9H₂O	11·74	17·03	11·60[3]				$Ibca$	2320	8	1·65[1]	1·63
3Na₂O . 2SiO₂ . 11H₂O	11·79	10·90	12·97				$Pbca$	1667	4	2·01[2]	2·00

(1) Baker, Woodward & Pabst (1933).
(2) From optical data; see text.
(3) *cf.* Lange & Stackelberg (1948): $a = 11·7_4$, $b = 16·8_8$, $c = 11·5_0$ Å.

Table 3. *Powder data for* Na₂O . SiO₂ . 5H₂O

d_{obs} (Å)	Intensity	hkl	d_{calc} (Å)	d_{obs} (Å)	Intensity
7·10	vvw	010	7·09	2·409	vw
6·64	vw	01$\bar{1}$	6·66	2·374	vvw
6·22	s	100	6·24	2·307	w
5·70	ms	1$\bar{1}$0	5·70	2·223	m
4·47	ms	011	4·47	2·197	vw
4·15	m	0$\bar{1}$2	4·16	2·163	m
4·07	m	110	4·07	2·161	vw
3·907	m	002	3·908	2·117	vvw
3·820	vvw	02$\bar{1}$	3·820	2·087	vvw
3·757	w	$\bar{1}$02	3·757	2·058	vvw
3·658	vvw	$\bar{1}$21	3·654	2·044	w
3·627	vw	$\bar{1}$20	3·632	2·012	w
3·328	s	02$\bar{2}$	3·330	1·959	w
3·273	s	$\bar{2}$10	3·278	1·900	s
3·153	s	111	3·154	1·878	vw
3·026	m	$\bar{1}$21	3·023	1·839	vvw
2·996	m	102	2·996	1·803	s
2·847	m	$\bar{2}$20 } 021 }	2·847 } 2·847 }	1·757	vvw
				1·728	vw
2·799	m			1·699	w
2·715	vs			1·674	w
2·652	vvw			1·648	m
2·626	w			1·640	vw
2·561	vvw			1·624	vw
2·514	vvw			1·581	m
2·472	m			1·554	w
				1·514	w
				1·501	m

Table 4. *Powder data for* Na₂O . SiO₂ . 6H₂O

d_{obs} (Å)	Intensity	hkl	d_{calc} (Å)	d_{obs} (Å)	Intensity
11·21	s	100	11·17	2·172	vw
6·19	vw	001	6·20	2·151	w
5·61	vvw	200	5·59	2·113	m
5·27	vw	110	5·26	2·090	ms
4·98	w	101	4·99	2·067	vvw
4·670	ms	$\bar{2}$01	4·665	2·054	vvw
4·300	vs	011	4·294	2·033	m
4·073	ms	210	4·075	1·994	m
3·824	m	111	3·826	1·959	w
3·672	ms	$\bar{2}$11	3·675	1·913	vvw
3·534	vw	301	3·536	1·891	w
3·184	vvw	211	3·188	1·873	vvw
3·162	w	$\bar{1}$02	3·162	1·863	vw
3·039	ms	$\bar{3}$11	3·040	1·826	m
2·975	w	020	2·979	1·800	w
2·934	m	301	2·932	1·775	w
2·878	vw	120	2·878	1·770	vvw
2·794	vs	$\bar{1}$12	2·793	1·757	w
2·684	vw	021	2·685	1·742	vw
2·672	m	212	2·671	1·727	w
2·631	ms	311	2·631	1·709	w
2·561	vs	112	2·561	1·682	vvw
2·513	s	$\bar{2}$21	2·511	1·668	vw
2·370	vw			1·655	vw
2·276	m			1·645	vvw
2·257	m			1·597	m

densities are accurately known. Excellent agreement was obtained by assuming:

$$R = 3·65 \,(O) + 1·63 \,(Na) + 0·00 \,(Si) + 0·00 \,(H)$$

where (O), (Na), (Si) and (H) are the respective numbers of atoms of each element in the formula whose weight M is used in the Lorentz–Lorenz equation. (*cf.* $R = 3·65 \,(O) + 3·25 \,(Ca) + 0·00 \,(Si) + 0·00 \,(H)$ for the anhydrous and hydrated calcium silicates.) For 3Na₂O . 2SiO₂ . 11H₂O, the density calculated is 2·01 g.cm⁻³; Z is therefore 4 and the X-ray density is 2·00 g.cm⁻³.

Results

The results of the X-ray studies are summarized in Table 2. Table 1 compares the X-ray results with the goniometric data; after suitable axial transformations (explained in the footnotes) agreement is good. The X-ray cell of Na₂O . SiO₂ . 5H₂O is chosen to be as nearly orthogonal as possible; that of Na₂O . SiO₂ . 8H₂O is chosen to give a conventional space group.

Tables 3–7 list the powder data. The pattern for Na₂O . SiO₂ . 5H₂O (Table 3) differs from both of those currently listed in the Powder Diffraction File (Cards no. 2–0465 and 3–0432); it is thought to be superior to them because it has been indexed satisfactorily. For the same reasons, the data for Na₂O . SiO₂ . 9H₂O (Table 6) are thought to be superior to those in the Powder Diffraction File (card no. 1–1007). The data for Na₂O . SiO₂ . 6H₂O (Table 4) agree substantially with those of Ryskin, Stavitskaya & Mitropolsky (1964). No powder data have previously been published for Na₂O .SiO₂ . 8H₂O (Table 5) or 3Na₂O . 2SiO₂ . 11H₂O (Table 7). Because of the size and comparative lack of symmetry of the unit cell of Na₂O . SiO₂ . 8H₂O, only the first few lines of the powder pattern could be indexed unambiguously. The unit-cell dimensions are therefore probably less accurate than those given for the other hydrates.

Discussion

The unit cells determined have no obvious common factor. The length 11·4–11·7 Å is encountered several times, but it is impossible to say whether this is significant.

Table 5. Powder data for $Na_2O . SiO_2 . 8H_2O$

d_{obs} (Å)	Intensity	hkl	d_{calc} (Å)	d_{obs} (Å)	Intensity
7·77	m	100	7·78	2·477	w
7·30	m	011	7·31	2·374	vw
5·20	vs	1̄21	5·21	2·333	w
4·68	m	1̄12	4·68	2·250	vw
4·25	m	2̄11	4·25	2·221	vvw
4·02	w	1̄22	4·02	2·171	w
		130 ⎫	3·91 ⎫	2·055	vvw
3·89	s	200 ⎬	3·89 ⎬	2·035	vw
		121 ⎭	3·88 ⎭	2·004	w
3·73	m	2̄21	3·73	1·936	w
3·66	w	022	3·66	1·867	vvw
3·49	w	2̄22	3·49	1·843	vvw
3·37	w	220	3·37	1·793	vw
3·02	vw			1·740	vvw
2·894	ms			1·730	vvw
2·757	vs			1·685	vvw
2·718	ms			1·648	vw
2·668	ms			1·638	vw
2·611	ms			1·615	vvw
2·600	ms			1·607	vvw

Table 6. Powder data for $Na_2O . SiO_2 . 9H_2O$

d_{obs} (Å)	Intensity	hkl	d_{calc} (Å)	d_{obs} (Å)	Intensity
8·51	m	020	8·51	2·217	vw
5·92	m	121	5·91	2·194	w
5·80	w	002	5·79	2·159	w
5·00	ms	211	5·00	2·126	mw
4·791	ms	022	4·791	2·030	mw
4·252	vvw	040	4·257	2·012	w
4·117	vvw	202	4·124	1·971	vvw
3·844	s	231	3·849	1·836	w
3·777	vvw	141	3·783	1·808	w
3·394	vw	321	3·398	1·772	vw
3·166	m	213	3·170	1·735	w
2·933	s	400	2·935	1·712	vw
2·894	vw	004	2·897	1·611	vw
2·836	m	060	2·838	1·549	vw
2·812	ms	332	2·816	1·508	vw
2·806	s	233	2·805	1·483	vvw
2·795	ms	341	2·795	1·457	vw
2·776	vs	420 ⎱ 114 ⎰	2·775 ⎱ 2·775 ⎰		
2·683	w	161	2·683		
2·617	vw	323 ⎱ 402 ⎰	2·616 ⎱ 2·618 ⎰		
2·597	vvw	204	2·598		
2·543	vvw	431	2·543		
2·347	w	352	2·348		
2·342	w	253	2·342		
2·308	w	314 ⎱ 343 ⎰	2·307 ⎱ 2·309 ⎰		
2·252	w	361	2·253		

Table 7. Powder data for $3Na_2O . 2SiO_2 . 11H_2O$

d_{obs} (Å)	Intensity	hkl	d_{calc} (Å)	d_{obs} (Å)	Intensity
6·82	s	111	6·81	2·270	vw
5·65	vvw	102	5·68	2·240	vw
5·47	vvw	020	5·45	2·176	w
5·02	m	021	5·03	2·136	vvw
4·627	m	121	4·623	2·124	vw
3·824	ms	221	3·825	2·089	vw
3·402	vvw	222	3·406	2·038	vvw
3·237	ms	004	3·240	2·031	vw
3·209	m	312	3·211	1·967	vw
3·060	ms	132	3·063	1·893	vvw
2·847	m	410	2·846	1·887	vvw
2·840	m	204	2·840	1·835	ms
2·791	w	232	2·793	1·789	vvw
2·773	w	—	—	1·785	vvw
2·728	w	040	2·728	1·765	vvw
2·707	m	133	2·707	1·757	vw
2·596	m			1·734	vvw
2·543	w			1·728	vvw
2·520	ms			1·682	w
2·455	w			1·663	vw
2·434	vw			1·598	w
2·410	vw			1·556	vw
2·373	vvw			1·543	vvw
2·344	vw			1·460	vvw
2·311	w			1·446	vw
2·301	m				

tetrahedra, not linked through a common oxygen atom. It seems likely that this is also true of the other hydrates. This agrees with the evidence quoted in the introduction.

The structures of three anhydrous sodium silicates [Na_2SiO_3 (Grund & Pizy, 1952), α-$Na_2Si_2O_5$ (Liebau, 1961) and β-$Na_2Si_2O_5$ (Grund, 1954)] have been determined to date. Na_2SiO_3 contains infinite $[SiO_3]^{2-}$ chains having a repeat distance of 4·8 Å. The two forms of $Na_2Si_2O_5$ contain $[Si_2O_5]^{2-}$ sheets formed by cross linking $[SiO_3]^{2-}$ chains; both their unit cells also show the chain repeat distance 4·8–4·9 Å. No such repeat distance is found in any of the hydrates. This strongly suggests that they do not contain $[SiO_3]^{2-}$ chains. A full structure analysis of $Na_2O . SiO_2 . 9H_2O$ based on three-dimensional data (to be described in part II) confirms that the silicon atoms occur in isolated

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