Peterson, 1953). The normal and deuterated bromide have essentially the same lattice parameter at 296°K and Levy & Peterson (1953) cite ~4·00 Å as the *a* value of ND_4Br at 77°K, which is in reasonable agreement with our value of 4·008 Å at that temperature. Secondly, the ratio $R = a(100°K)/a(295°K)$ is almost identical for NH_4Cl and NH_4Br in its cubic phase. The value of *R* obtained from our NH_4Br measurement is $0{\cdot}9882_7$, while the *R* value calculated from the NH_4Cl data of Pilbrow & Spaeth (1967) is $0{\cdot}9881_3$. A more detailed comparison of this sort is not possible since no reliable NH_4Cl lattice parameters have been reported below 100°K.

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The application of some liquid scattering functions to X-ray data from the zeolite complex *m*-dichlorobenzene–Ni-faujasite.

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The application of formulae for the average scattering of X-rays from *m*-dichlorobenzene molecules and exchangeable nickel cations uniformly distributed in the intracrystalline channels of the zeolite natural faujasite is illustrated. Application of these formulae to the actual X-ray data revealed that the sorbed *m*-dichlorobenzene molecules and previously unlocated nickel cations form a liquid or near liquid in the zeolite channels.

Introduction

During a recent crystal structure analysis of Ni faujasite saturated with *m*-dichlorobenzene and of Mn faujasite saturated with 1-chlorobutane (Simpson & Steinfink, 1969) it became evident that the sorbed molecules form a liquid or near-liquid in the interconnected supercages defined by the aluminosilicate framework. It is known that the centers of these cages are at definite crystallographic sites (Bergerhoff, Baur & Nowaki, 1958; Baur, 1964). The liquid scattering is modified by this periodic arrangement, resulting in a significant contribution by the sorbed guest molecules and unlocated nickel cations to the low order structure factors.

During the course of the analysis of the low order X-ray data for the *m*-dichlorobenzene complex, many models were tried in an effort to elucidate possible preferred orientation and ordering of the guest molecules before it was finally concluded and demonstrated that the best model is one which postulates an essentially uniform distribution of the electron density of these molecules in the channels formed by the supercages. In this paper we present the scattering equations used for the uniformly distributed *m*-dichlorobenzene molecules and nickel cations in some of the trial models and the final model, and the effect of each model on the low order structure factors. Only the *m*-dichlorobenzene complex is considered since the analysis of the 1-chlorobutane complex was very similar.

Before reaching the stage of analysis in which the models presented here were tried, it was established that there were about four molecules of *m*-dichlorobenzene per supercage and that about 0·9 nickel cations were uniformly distributed in each supercage as well as in each sodalite cage. The space group is *Fd*3*m*. The centers of the supercages, the sodalite cages, and the hexagonal prisms (which connect the sodalite cages together) are Wyckoff positions *b*, *a* and *c* respectively, and their respective approximate free dimensions are 12, 7 and 3 Å.

Formulae for the average scattering from atoms distributed uniformly throughout the volume of a sphere and on a circular arc have been given by King & Lipscomb (1953), and the formula for the average scattering from an atom uniformly distributed over the surface of a sphere has been given by Verweel & Bijvoet (1938) and Zachariasen (1945). Derivations and graphical presentations of the modifying functions in some of these formulae are given by James (1950).

The hydrogen atoms were neglected in the analysis.

Notation

Let $\mathbf{S}$ = the reciprocal lattice vector of the reflection considered (Å^{-1}).

$\mathbf{r}$ = the position vector of the center of the sphere of distribution (Å).

$\Sigma_a = \sum_a \exp[2\pi i \mathbf{S} \cdot \mathbf{r}_a]$, the vector summation over the centers of the sodalite cages.

$\Sigma_b = \sum_b \exp[2\pi i \mathbf{S} \cdot \mathbf{r}_b]$, the vector summation over the centers of the supercages.

$\Sigma_c = \sum_c \exp[2\pi i \mathbf{S} \cdot \mathbf{r}_c]$, the vector summation over the centers of the hexagonal prisms.

R_a = the radius of distribution for the sodalite cage.

R_b = the radius of distribution for the supercage. In the case of distribution between two concentric spheres in the supercage, the larger radius is R_2 and the smaller is R_1.

R_c = the radius of distribution for the hexagonal prisms.

$U_{\mathrm{C}} = 1{\cdot}4$ Å, the distance from the center of the benzene ring of a *m*-dichlorobenzene molecule to the centers of the six component carbon atoms.

$U_{\mathrm{Cl}} = 3{\cdot}1$ Å, the distance of the centers of the two chlorine atoms from the center of the benzene ring in a *m*-dichlorobenzene molecule.

$\mu = 4\pi \sin\theta/\lambda$, where θ is the Bragg angle and λ is the wavelength of the X-radiation used (Å).

$\mathbf{N}$ = a normal to the plane of the benzene ring in a *m*-dichlorobenzene molecule.

$\psi = \cos^{-1}[(\mathbf{S} \cdot \mathbf{N})/SN]$, the angle between $\mathbf{N}$ and $\mathbf{S}$.

f = the temperature uncorrected scattering factor. The scattering factors for carbon, chlorine, and nickel atoms respectively are denoted by f_{C}, f_{Cl} and f_{Ni}.

$\mathbf{g}$ = the average complex scattering. The average scattering from *m*-dichlorobenzene molecules is denoted by $\mathbf{g}_b^m$. The average scattering from the uniformly distributed nickel atoms in the sodalite cages and supercages is denoted by $\mathbf{g}_a^{\mathrm{Ni}}$ and $\mathbf{g}_b^{\mathrm{Ni}}$ respectively.

Formulae

In the descriptions, 'molecule' refers to *m*-dichlorobenzene. In the equations which postulate a random orientation of the molecules, the reference point about which each was so oriented was the center of its benzene ring.

(1) Four molecules per supercage randomly oriented and with their centers distributed uniformly over the surface of a sphere in the supercage:

$$\mathbf{g}_b^m = \Sigma_b \left\{ 4\left[6 f_{\mathrm{C}} \frac{\sin \mu U_{\mathrm{C}}}{\mu U_{\mathrm{C}}} + 2 f_{\mathrm{Cl}} \frac{\sin \mu U_{\mathrm{Cl}}}{\mu U_{\mathrm{Cl}}}\right] \cdot \left[\frac{\sin \mu R_b}{\mu R_b}\right]\right\}.$$

(2) One molecule facing each of the four unique $\langle 111 \rangle$ directions in each supercage, with the molecules randomly oriented in the planes of their benzene rings and having their centers distributed uniformly over the surface of a sphere in the supercage:

$$\mathbf{g}_b^m = \Sigma_b \left\{ \sum_{1=i}^{4} [6 f_{\mathrm{C}} J_0(\mu U_{\mathrm{C}} \sin \psi_i) + 2 f_{\mathrm{Cl}} J_0(\mu U_{\mathrm{Cl}} \sin \psi_i)] \cdot \left[\frac{\sin \mu R_b}{\mu R_b}\right]\right\}.$$

(3) Four molecules per supercage randomly oriented and with their centers distributed uniformly throughout the volume between concentric spheres in the supercage:

$$\mathbf{g}_b^m = \Sigma_b \left\{ 4\left[6 f_{\mathrm{C}} \frac{\sin \mu U_{\mathrm{C}}}{\mu U_{\mathrm{C}}} + 2 f_{\mathrm{Cl}} \frac{\sin \mu U_{\mathrm{Cl}}}{\mu U_{\mathrm{Cl}}}\right] \cdot \left[\frac{3}{\mu^3 (R_2^3 - R_1^3)}\right] [\sin \mu R_2 - \sin \mu R_1 - \mu R_2 \cos \mu R_2 + \mu R_1 \cos \mu R_1]\right\}.$$

(4) Four molecules per supercage randomly oriented in the plane of the benzene ring and with their centers distributed uniformly over the surface of a sphere while the normals to the planes of the benzene rings remain directed toward the center of the sphere:

$$\mathbf{g}_b^m = \Sigma_b \left\{ 4 \left[6 f_{\mathrm{C}} \int_0^{\pi/2} \cos(\mu R_b \cos \psi) \cdot J_0(\mu U_{\mathrm{C}} \sin \psi) \sin \psi \, d\psi + 2 f_{\mathrm{Cl}} \int_0^{\pi/2} \cos(\mu R_b \cos \psi) J_0(\mu U_{\mathrm{Cl}} \sin \psi) \sin \psi \, d\psi \right]\right\}.$$

The integrals in this equation were approximated numerically.

(5) The individual carbon and chlorine atoms in four molecules uniformly distributed throughout a sphere in each supercage:

$$\mathbf{g}_b^m = \Sigma_b \left\{ [24 f_{\mathrm{C}} + 8 f_{\mathrm{Cl}}] \cdot \left[\frac{3}{(\mu R_b)^3} (\sin \mu R_b - \mu R_b \cos \mu R_b)\right]\right\}.$$

(6) A nickel atom uniformly distributed throughout a sphere in each supercage:

$$\mathbf{g}_b^{\mathrm{Ni}} = \Sigma_b \left\{ f_{\mathrm{Ni}} \left[\frac{3}{(\mu R_b)^3} (\sin \mu R_b - \mu R_b \cos \mu R_b)\right]\right\}.$$

(7) A nickel atom uniformly distributed throughout a sphere in each sodalite cage – the same as formula (6), except Σ_a replaces Σ_b and R_a replaces R_b.

(8) A nickel atom uniformly distributed throughout a sphere in each hexagonal prism – the same as formula (6) except Σ_c replaces Σ_b and R_c replaces R_b.

Models and results

This section presents a description of four selected trial models and the final model used to describe the *m*-dichlorobenzene molecules and unlocated nickel atoms in *m*-dichlorobenzene–Ni-faujasite. Table 1 shows the observed amplitudes and calculated structure factors for the framework only, as well as for the framework plus each of the five selected models, for 16 low order reflections. The quantity R_{16} in the Table is $\{\Sigma||F_o| - |F_c||\}/\{\Sigma|F_o|\}$ for these reflections.

Table 1. *Observed amplitudes and calculated structure factors for* 16 *low order reflections using selected models for m-dichlorobenzene-*Ni*-faujasite*

			F_c				
hkl	$\|F_o\|$	Framework	A^*	B^*	C^*	D^*	E^*
220	91	411	100	146	74	416	108
222	64	−111	−111	−111	−111	−111	−42
311	240	351	245	204	243	164	263
331	487	−669	−531	−504	−519	−569	−520
333	143	157	231	251	238	136	155
400	235	−271	−232	−234	−241	−168	−219
440	774	−787	−788	−758	−765	−659	−712
444	325	−299	−304	−355	−321	−340	−302
511	459	507	581	571	588	487	519
533	1014	−938	−945	−936	−947	−885	−925
551	302	300	306	305	302	310	290
555	1533	−1421	−1438	−1443	−1430	−1378	−1411
620	355	266	271	297	295	373	296
622	191	−119	−119	−119	−119	−119	−84
642	587	−509	−513	−531	−521	−479	−498
660	583	712	714	725	717	795	731
R_{16}		0·183	0·126	0·125	0·114	0·198	0·121

* Structure factors now include the contribution of the assumed model in addition to the silicate framework.

Model *A*: four molecules per supercage according to formula 1 with R_b = 4·0 Å, 0·9 Ni atoms per supercage with R_b = 4·0 Å, and 0·9 Ni atoms per sodalite cage with R_a = 2·3 Å.

Model *B*: four molecules per supercage according to formula 2 with R_b = 4·0 Å. The disposition of the nickel atoms is the same as in model *A*.

Model *C*: four molecules per supercage according to formula 3 with R_2 = 4·3 Å and R_1 = 3·2 Å, 0·9 Ni atoms in each supercage with R_b = 5·5 Å, and 0·9 Ni atoms in each sodalite cage with R_a = 2·3 Å.

Model *D*: four molecules per supercage according to formula 4 with R_b = 4·0 Å. The disposition of the Ni atoms is the same as in model *A* except 0·6 atoms were used instead of 0·9 in each cage.

Model *E*: final model. Four molecules per supercage according to formula 5 with R_b = 5·8 Å, 0·9 Ni atoms per supercage with R_b = 3·5 Å, 0·6 Ni atoms per sodalite cage with R_a = 2·3 Å, and 0·1 Ni atom in each hexagonal prism with R_c = 1·5 Å.

In the initial trial models (which include models *A* through *D*) a temperature factor was not used because this factor has little effect on the liquid scattering equations, which are intrinsically rapidly damped. However, a temperature factor of $B = 20$ Å^2 was used in the final model *E*. This model was contrived, after a detailed consideration of the graphs of the various scattering functions for both molecular and atomic representations of the sorbed *m*-dichlorobenzene, to provide a better weighted fit of the data than the previous trial models, *i.e.* an improved value of $\{w(|F_o|-|F_c|)^2\}$ where w is $1/[\sigma(F)]^2$. The treatment of the *m*-dichlorobenzene molecules in terms of their constituent atoms and the incorporation of a high temperature factor thus constituted a 'refinement' in the description of the electron density in the zeolitic channels. The *R* values for the best initial trial models varied between 0·101 and 0·103 while the values for *wR* varied between 0·106 and 0·110. ($R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$, $wR=[\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$. The values obtained with the final model *E* were $R = 0{\cdot}098$ and $wR = 0{\cdot}099$.

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