Intraionic Structure of HSO_4^- and Alkali Cation Configuration in Molten $NaHSO_4$ and $KHSO_4$

K. Fukushima, M. Murofushi *, M. Oki, K. Igarashi **, J. Mochinaga ***, and Y. Iwadate

Department of Materials Science, Faculty of Engineering, Chiba University, Yayoi-cho, Inage-ku, Chiba 263, Japan

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The short range structure of molten $NaHSO_4$ (I) and $KHSO_4$ (II) was estimated by X-ray diffraction. The polyatomic anion, HSO_4^-, in both molten salts was found to have a distorted tetrahedral structure in which the bond lengths of S–O and S–OH were 1.45 Å and 1.53 Å in (I) and 1.46 Å and 1.56 Å in (II), respectively. The coordination number of the Na^+ or K^+ around the HSO_4^- was evaluated to be about unity. The semi-empirical molecular orbital calculations by the MNDO-MOPAC method were applied to the determination of the intraionic structure of the HSO_4^- and the bond lengths of S–O and S–OH were computed to be 1.528 Å and 1.666 Å, respectively, supporting qualitatively that the HSO_4^- forms a rather distorted tetrahedron.

Introduction

Several structural investigations on crystalline $NaHSO_4$ and $KHSO_4$ have so far been reported. Loopstra and MacGillavry [1] pointed out that the four S–O bond lengths in HSO_4^- are all equal. On the contrary, Sonneveld and Visser [2] and Cruickshank [3] concluded that the S–O(H) bond was longer than the other three S–O bonds. Ohno and Furukawa [4] and Morikawa et al. [5] examined the structure of molten Na_2SO_4 and estimated the coordination number of Na^+ around the SO_4^{2-} tetrahedron to be 3.7, where three Na^+ occupy corner-sites and the others face-sites. Miyake et al. [6] investigated the structure of molten K_2SO_4 and concluded that four K^+ are situated around the SO_4^{2-} tetrahedron, that is, one out of four K^+ practically occupies corner-sites and the others edge-sites. Thus, it may be of much interest to investigate the local structure of molten $NaHSO_4$ and $KHSO_4$, since the structure of HSO_4^- is more complicated than that of SO_4^{2-}. There is, however, some difficulty in determining the accurate position of hydrogen in HSO_4^-. To overcome this problem, procedures such as neutron diffraction, molecular dynamics simulation, and molecular orbital calculations are, in general, quite useful. Recently, the semi-empirical MNDO SCF-MO method has been established as a practical procedure for studying the structure and chemical behaviour of molecules or ions. The results achieved are comparable with those from ab initio MO calculations.

In this work, the MNDO-MOPAC method was used to derive the local structure of molten $NaHSO_4$ and $KHSO_4$. The results are compared with those determined by X-ray diffraction measurements.

Experimental

Reagent grade $KHSO_4$ was dried in a desiccator for a week with phosphorus pentoxide. Anhydrous $NaHSO_4$ used in this work was prepared by heating $NaHSO_4 \cdot H_2O$ at about 463 K until the distillate was changed to be acid. The XRD measurements of molten $NaHSO_4$ and $KHSO_4$ were carried out at 478 K and 508 K, respectively. The MoKα radiation with the wavelength of 0.7107 Å was used. The diffracted beam which was monochromatized with curved graphite. The scattered intensities were recorded with a scintillation counter in the range of $0.918 \leqq S/\text{Å}^{-1} \leqq 14.3$. The parameter S is defined by $S = 4\pi \sin\theta/\lambda$, where θ is the Bragg angle and λ the wavelength of the radiation. The intensity data were corrected for background, polarization, absorption and Compton scattering, and normalized to the independent scattering factor for the stoichiometric unit in

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* Asahi Glass Corporation Ltd.; Yawatahara 4-2837-11, Yonezawa 992-11, Japan.

** Government Industrial Research Institute Nagoya; Hirate-cho 1-1, Kita-ku, Nagoya 463, Japan.

*** Formerly of Chiba University.

Reprint requests to Prof. Y. Iwadate, Department of Materials Science, Faculty of Engineering, Chiba University, Yayoi-cho, Inage-ku, Chiba 263, Japan.

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accordance with the usual procedure [7]. The radial distribution function $G(r)$ and the reduced intensity function $S \cdot i(S)$ were calculated, the definitions of which have previously been given in detail elsewhere [8]. Analytical parameters for the calculation of $D(r)$ and $G(r)$ are listed in Table 1. The densities of molten $NaHSO_4$ and $KHSO_4$ were measured by dilatometry and expressed by the empirical equations,

$$\varrho = 2.659 - 9.26 \times 10^{-4} \times T \text{ for } NaHSO_4,$$

$$\varrho = 2.579 - 8.65 \times 10^{-4} \times T \text{ for } KHSO_4,$$

where the temperature T is given in K. The structure of the melts is described by radial distribution functions in the r-space and structure functions (structure factors) in the S-space.

Molecular orbital calculations of the HSO_4^- in terms of the MNDO method were made with the MOPAC Ver. 6.02 program [9].

Results and Discussion

As shown in Fig. 1, similar peak patterns in $G(r)$ were obtained for molten $NaHSO_4$ and $KHSO_4$ except for the range of $r = 2$ to 3 Å, for instance, the first peak and the second one being centered at 1.05 Å and 2.45 Å, respectively. Inspecting the profiles of the first peaks precisely, asymmetry was observed in both cases. According to the crystal radii by Pauling [10], the radii of S^{6+} and O^{2-} are 0.29 Å and 1.40 Å, respectively. Similarly, the corresponding ionic radii were determined by Shannon [11] to be 0.12 Å and 1.40 Å, respectively. The first peak could therefore be thought to correspond to the S–O and S–O(H) pairs. By integrating the corresponding peak area, the coordination number of O atom around S atom was indeed estimated to be about 4. Moreover, the second peak in $G(r)$ was assignable to the distance of the intraionic O–O pair. The above results and the radius ratios of the component species suggest that there exist HSO_4^- or SO_4^{2-} tetrahedra in molten $NaHSO_4$ and $KHSO_4$.

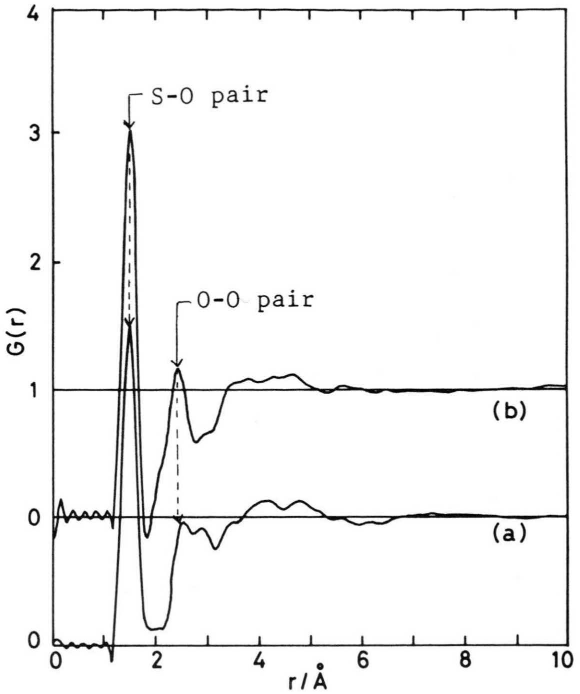

Fig. 1. Total radial distribution function $G(r)$ of the molten hydrogen sulfates; (a) $KHSO_4$: 508 K, (b) $NaHSO_4$: 478 K.

Table 1. Parameters for the calculation of $D(r)$ and $G(r)$.

	$KHSO_4$	$NaHSO_4$
Temperature/K	508	478
Density/g · cm^{-3}	2.140	2.216
ϱ_0/Å^{-3}	0.00946	0.01112
Effective electron number		
$\overline{K_H}$	0.2644	0.2646
$\overline{K_K}$	21.9435	
$\overline{K_{Na}}$		11.2476
$\overline{K_S}$	18.0523	19.1961
$\overline{K_O}$	6.9345	7.3225
S_{max}/Å^{-1}	14.3	14.3

The structures of solid $NaHSO_4$ [2] and $KHSO_4$ [3] have been reported such that one S–O(H) distance is longer than the remaining S–O distances in the HSO_4^- tetrahedron which exists surely in the solid state. Unfortunately, no information of the O–H bonding could be derived from the XRD experiments. In order to learn whether a tetrahedral SO_4^{2-} ion or a distorted tetrahedral HSO_4^- exist in molten $NaHSO_4$ and $KHSO_4$, the correlation method was applied to the $S \cdot i(S)$ functions. The phase in the $S \cdot i(S)$ intensity profile calculated for SO_4^{2-} was shifted to an S-region larger by 0.2 Å^{-1} than that for HSO_4^-, indicating that HSO_4^- was hardly dissociated to SO_4^{2-} and H^+.

So far it has been reported that $S_2O_7^{2-}$ was formed by dimerization after the dehydration of HSO_4^- in the temperature range of 573 K to 973 K [12]. In the temperature range of this work, it was quite difficult to evaluate the contribution of the S–S atomic pair in

Table 2. Least-squares fitted structural parameters of coordination number, n_{ij}, average interatomic distance, r_{ij}, and root mean square displacement, $\langle \Delta r_{ij}^2 \rangle^{1/2}$ for the model structure of molten $NaHSO_4$ and $KHSO_4$.

Model	i	j	$NaHSO_4$			$KHSO_4$		
			n_{ij}	r_{ij}/Å	$\langle \Delta r_{ij}^2 \rangle^{1/2}$/Å	n_{ij}	r_{ij}/Å	$\langle \Delta r_{ij}^2 \rangle^{1/2}$/Å
(1) Intraionic	S	O	3	1.45	0.111	3	1.46	0.109
	S	O(H)	1	1.53	0.121	1	1.56	0.107
	O	O	6	2.38	0.139	6	2.40	0.121
	O	O	6	2.41	0.139	6	2.41	0.117
(2) Interionic								
Face-site	M	S	1	2.59	0.214	1	2.95	0.257
	M	O	3	2.42	0.200	3	2.78	0.245
	M	O	1	4.04	0.245	1	4.40	0.300
Edge-site	M	S	1	2.89	0.224	1	3.38	0.265
	M	O	2	2.42	0.200	2	2.78	0.245
	M	O	2	4.04	0.245	2	4.40	0.300
Corner-site	M	S	1	3.87	0.245	1	4.23	0.300
	M	O	1	2.42	0.200	1	2.78	0.245
	M	O	3	4.54	0.265	3	4.90	0.316

O(H): Oxygen bonding to Hydrogen, M: Alkali metal ion.

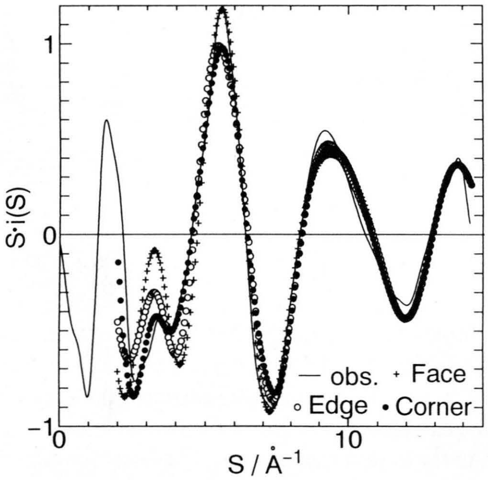

Fig. 2. Reduced intensity functions $S \cdot i(S)$ of molten $NaHSO_4$ at 478 K.

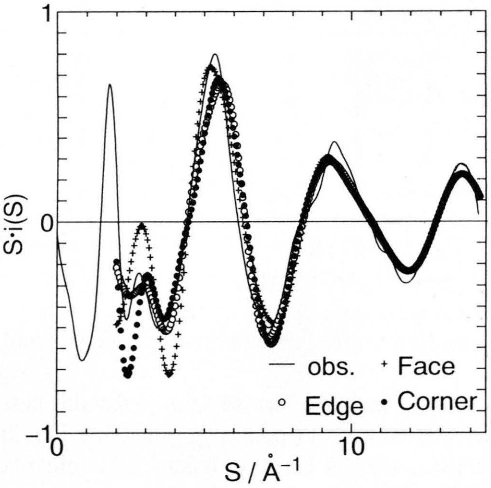

Fig. 3. Reduced intensity functions $S \cdot i(S)$ of molten $KHSO_4$ at 508 K.

$S \cdot i(S)$. It can be concluded from the above results that there are stable distorted tetrahedral HSO_4^- ions in molten $NaHSO_4$ and $KHSO_4$ as well as in the solid state. The coordination numbers of Na^+ or K^+ around HSO_4^-, the corresponding interatomic distances, and the root mean square displacements were considered for three typical models, in which the cations can be located: i) face-site of HSO_4^-, adjacent to the face of the HSO_4^- tetrahedron, ii) edge-site, and iii) corner-site. In all cases, it should be noted that the cation tend to be situated at the position far from the hydrogen, being quite natural when considering the charge distribution of the pair cation/polyatomic anion. The parameters of the most probable structural model for molten $NaHSO_4$ and $KHSO_4$ are listed in Table 2, and the observed and calculated $S \cdot i(S)$ curves are shown in Figs. 2 and 3. The structure of molten Na_2SO_4 and K_2SO_4 has been investigated in detail by Ohno and Furukawa [4], Morikawa et al. [5] and Miyake et al. [6]. The coordination numbers of Na^+ or K^+ around SO_4^{2-} were estimated to be 3.7 [5] and 4 [6] for the respective pure melts. In contrast, the corresponding coordination numbers of the cation around the anion obtained for $NaHSO_4$ and $KHSO_4$ by the least squares method were almost unity in both cases. These findings indicate that a cation occupies

Table 3. Intraionic structure of HSO_4^- by MNDO-MOPAC calculation.

Bond length/Å

Pair	S–O	pair	O–O	pair	O–O	pair	O–H
1–2	1.529	2–3	2.578	3–4	2.579	5–6	0.941
1–3	1.527	2–4	2.557	3–5	2.516	2–6	2.756
1–4	1.529	2–5	2.513	4–5	2.512	3–6	3.372
1–5	1.666					4–6	2.732

Bond angle

∠2–1–3	115.06°	∠2–1–4	113.48°
∠2–1–5	103.64°	∠1–5–6	115.15°

Numerics correspond to the notation in Figure 4.

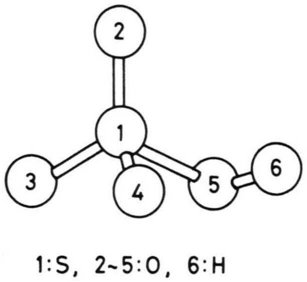

Fig. 4. Model of HSO_4^-.

Table 4. Comparison of bond lengths in HSO_4^-.

State	System	S–O(H)/Å	S–O/Å	Method	References
Solid	$NaHSO_4$	1.58	1.46	XRD	Sonneveld and Visser [2]
	$KHSO_4$	1.52	1.52	XRD	Loopstra and MacGillavry [1]
	$KHSO_4$	1.56	1.47	*	Cruickshank [3]
Melt	$NaHSO_4$	1.53	1.45	XRD	this work
	$KHSO_4$	1.56	1.47	XRD	this work
Discrete ion	HSO_4^-	1.666	1.528	MO	this work

* Refinement of the data given by Loopstra and MacGillavry.

only one position among the corner-site, face-site and edge-site.

For $NaHSO_4$ melt, the corner-site gives the best agreement with the experimental $S \cdot i(S)$ (see Fig. 2) but for $KHSO_4$ melt, it is more difficult to confirm a particular location (see Figure 3). The correlation functions, $G(r)$'s, of three models, calculated from the result of the least squares method, reproduced the observed $G(r)$ very well. The structure discussed as face-site, edge-site, and corner-site made a great contribution to the intensity profile of $S \cdot i(S)$ in the range of $2 \leqq \text{Å}^{-1} \leqq 4$, particularly when the cation occupied the face-site.

The intraionic structure of HSO_4^- calculated with MNDO-MOPAC is illustrated in Fig. 4 and tabulated in Table 3. The bond lengths of S–O were not all equal, that is, the S–O(H) bond length, 1.666 Å, was longer by 0.14 Å than the other three S–O bond lengths (average value: 1.528 Å). The twist angle of O(3) · S(1) · O(5) · H(6) was computed to be −178.4°, where the indexes of the atoms refer to Figure 4. The HSO_4^- structure derived from the MOPAC calculation was found to be a rather distorted SO_4 tetrahedron with an OH bonding. Qualitatively, it is in fair agreement with the experimental structural data, although the calculated bond lengths are systematically longer than the experimental ones. The bond length of O–H was evaluated to be 0.94 Å, which was impossible to determine from X-ray diffraction. A comparison of the bond length data is given in Table 4, supporting that the intraionic structure of HSO_4^- determined by XRD remains the same in the melt and the solid state.

Conclusions

1. Distorted tetrahedral HSO_4^- exists in molten $NaHSO_4$ and $KHSO_4$, the coordination number of the alkali cation around HSO_4^- being estimated to be unity.
2. The cation is located at one of the sites described as corner, face, and edge site, especially for $NaHSO_4$ melt with a preference for the corner site.
3. The MNDO MO calculations support the distorted HSO_4^- model derived from X-ray diffraction.

Acknowledgements

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