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Diffraction Pattern and Models of Liquid Antimony Trichloride*

E. Johnson, A. H. Narten, W. E. Thiessen,
and R. Triolo

Chemistry Division
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37830

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Neutron and x-ray diffraction data for liquid SbCl_3 at 80°C are presented and discussed. The liquid consists of discrete molecules with an Sb-Cl distance of $2.35 \text{ \AA}$ and a Cl-Sb-Cl angle of 96° . The diffraction data are analyzed to yield structure and correlation functions for intermolecular $\text{Sb}\cdots\text{Sb}$, $\text{Sb}\cdots\text{Cl}$, and $\text{Cl}\cdots\text{Cl}$ interactions. These curves yield directly some valuable insight into the nature of the strong orientational correlations present in liquid SbCl_3 .

The data are also used to test site-site interaction models for molecular fluids. The relative role of repulsive and attractive forces for the structure of liquid SbCl_3 is discussed.

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Despite its complicated chemistry¹, antimony trichloride above its melting temperature is a molecular liquid not unlike water in its physical properties. Because of its low auto-ionization and its high dielectric constant (33.2 at 75°C)², liquid SbCl_3 like water is a good solvent³ for inorganic solutes.

We have previously studied liquid SbCl_3 with both x-rays and thermal neutrons at 80°C, just above the melting point of 73.4°C. The diffraction data have been analyzed⁴ to yield the molecular structure, which is pyramidal with a bond distance of 2.35 Å* and a bond angle of 96°. The final result of the data reduction is the distinct scattering function $S_d(k)$, defined below, which contains information about intermolecular correlations in the liquid.

In this discussion, we will explore two ways of interpreting the experimental scattering functions. The first is an approximate analysis which provides an estimate of the intermolecular atom pair distribution functions. The second method is better founded but less direct. In this we start with a model of the intermolecular potential function and, using statistical mechanical theories of the liquid state, compute the x-ray and neutron scattering functions. Using this procedure, we have not been able to find a model for liquid SbCl_3 which agrees with the diffraction data. Our final interpretation of the spatial correlations which exist in liquid SbCl_3 is therefore based on the atom pair distribution functions derived from the experimental data.

*1 Å = 10^{-10} m.

ANALYSIS OF THE DIFFRACTION DATA

Before proceeding with the details of our analysis, it is useful to discuss the types of spatial correlations that will be used.

The first description is based upon considering the atom as the basic scattering unit, and defining atom-atom pair distribution functions $g_{\alpha\gamma}(r)$ so that $\rho^2 g_{\alpha\gamma}(r)$ is the probability density that atom α of one molecule is at the origin and that atom γ of another molecule is at r . Here ρ is the bulk molecular density. For SbCl_3 , three distribution functions are needed, $g_{\text{SbSb}}(r)$, $g_{\text{SbCl}}(r)$, and $g_{\text{ClCl}}(r)$.

The other description takes the molecule as the basic scattering and structural unit. Let the symbol X_1 denote the set of all coordinates needed to specify the position and orientation of a molecule. The function $\rho^2 g(X_1, X_2)$ is the probability density that one molecule is at X_1 and that another molecule is at X_2 . Here $g(X_1, X_2)$ is the pair distribution function. It is convenient to expand the correlation function $h(X_1, X_2) \equiv g(X_1, X_2) - 1$ in a complete set of orthonormal polynomials in the orientation variables⁵. With this representation it is possible to display the multidimensional correlation function $h(X_1, X_2)$ as a set of one-dimensional coefficients $h_{\mu\nu}^{mn\ell}(r)$. The Fourier-Bessel transform of the invariant⁶ coefficients,

$$\hat{h}_{\mu\nu}^{mn\ell}(k) = 4\pi i^{-1} \int_0^\infty dr r^2 j_\ell(kr) h_{\mu\nu}^{mn\ell}(r), \quad (1)$$

is in turn related to the irreducible⁷ coefficients,

$$\hat{h}_{\mu\nu,0}^{mn}(k) = \sum_\ell \begin{bmatrix} mn\ell \\ 000 \end{bmatrix} \hat{h}_{\mu\nu}^{mn\ell}(k) \quad (2)$$

where the Wigner 3-j symbols appear.

The distinct structure function accessible from diffraction data⁴ can now be written in the compact notation

$$S_d(k) = \rho \sum_{\substack{mn \\ \mu\nu}} (-)^{\nu} a_{\mu}^m a_{\nu}^n \mathcal{H}_{\mu\nu,0}^{mn}(k) . \quad (3)$$

The molecular scattering factors $a_{\mu}^m(k)$, with k the momentum transfer coordinate, can be calculated⁷ from the atomic scattering factors if the molecular structure is known. The series of Eq. (3) converges reasonably quickly if the coefficients $\mathcal{H}_{\mu\nu,0}^{mn}(k)$ and/or the products $a_{\mu}^m a_{\nu}^n$ with either $m \neq 0$ or $n \neq 0$ are small, in which case the leading spherical term, $\mathcal{H}_{00,0}^{00}(k)$, in Eq. (3) will dominate the scattering function $S_d(k)$. The physical condition for this is that we are dealing with randomly oriented molecules and/or with molecules having a nearly spherical distribution of scattering density. The first case has never been observed, but the second condition holds for the electron density distribution in a number of molecules.

We have computed the molecular scattering factors a_{μ}^m for the SbCl_3 molecule, and the numbers confirm that for x-ray (but not neutron) scattering only those terms in Eq. (3) with $n = 0$ or $m = 0$ and with μ and ν equal to zero are relevant. Hence, we may write Eq. (3) as

$$S_d(k)/|a_0^0(k)|^2 = \rho \mathcal{H}_{00,0}^{00}(k) + 2\rho \sum_{m \neq 0} (a_0^m/a_0^0) \mathcal{H}_{00,0}^{m0}(k) \quad (4)$$

with

$$\mathcal{H}_{00,0}^{00}(k) = \hat{h}_{00}^{000}(k) = \hat{h}_{\text{SbSb}}(k) . \quad (4a)$$

The quantity $\hat{h}_{\text{SbSb}}(k)$ is the Fourier transform of the atom pair correlation function $h_{\text{SbSb}}(r) \equiv g_{\text{SbSb}}(r) - 1$, and the right hand equality in

Eq. (4a) holds because we have chosen the Sb atom as the origin in the molecular scattering factor expansion.

The function $S_d^*(k) \equiv S_d(k)/|a_0^0|^2$ derived from x-ray scattering is shown in Fig. 1 (circles). Also shown (dashed curve) is the computed nonspherical part of the scattering, $A_{NS}(k) \equiv 2 \sum_{m \neq 0} (a_m^m/a_0^0)$. The function $A_{NS}(k)$ has its first maximum near $1.5 \text{ \AA}^{-1}$ where the experimental function $S_d^*(k) = 0$. We conclude from this and from other empirical evidence^{7,8} that the first peak near $1.9 \text{ \AA}^{-1}$ in $S_d^*(k)$ contains almost no contribution from the nonspherical part (4a) of the pair distribution function. At values of $k > 4 \text{ \AA}^{-1}$, the nodes of the two curves in Fig. 1 coincide almost exactly and we conclude that the function $\hat{h}_{SbSb}(k)$ decays rapidly to zero value with increasing k . Based on these observations we may assume that the approximation

$$S_d^*(k) \approx \rho \hat{h}_{SbSb}(k), \quad k \gtrsim 4 \text{ \AA}^{-1} \quad (5)$$

will provide a realistic estimate of the structure function for Sb-Sb interactions from the x-ray data.

The function $S_d^*(k)$ was terminated at $3.6 \text{ \AA}^{-1}$ where the curve (Fig. 1) goes through zero value. The thus truncated function $S_d^*(k)$ was Fourier transformed to yield an estimate of the atom pair distribution function $g_{SbSb}(r)$. The curve thus obtained showed a positive peak near the origin and a sizeable negative peak near $2 \text{ \AA}$. The first feature may be ascribed to the truncation of $S_d^*(k)$. We assign the second feature to small nonspherical contributions to $S_d^*(k)$ below the truncation value of $3.6 \text{ \AA}^{-1}$. We have eliminated these features by requiring $g_{SbSb}(r)$ to assume zero value for $r < 3 \text{ \AA}$, a reasonable distance for the closest approach between

SbCl_3 molecules⁴. The inverse transform of the idealized function $h_{\text{SbSb}}(r)$ will now be taken as a realistic estimate of the function $\hat{h}_{\text{SbSb}}(k)$.

The functions $\hat{h}_{\text{SbCl}}(k)$ and $\hat{h}_{\text{ClCl}}(k)$ can now be determined from the two structure functions derived in our previous analysis⁴ of x-ray and neutron scattering from liquid SbCl_3 . The distinct structure functions, in terms of atom pair interactions, are

$$H_d^{X,N}(k) = M(k) [f_{\text{Sb}}^2 a_{\text{SbSb}} + 6f_{\text{Sb}} f_{\text{Cl}} a_{\text{SbCl}} + 9f_{\text{Cl}}^2 a_{\text{ClCl}}] \quad (6)$$

With $M(k) = [f_{\text{Sb}} + 3f_{\text{Cl}}]^{-2}$, $a_{\alpha\gamma}(k) \equiv \rho \hat{h}_{\alpha\gamma}(k)$, and $f_{\alpha}(k)$ the atomic scattering factor of atom α . We note that the Sb-Sb interactions contribute only 24% to the x-ray structure function and 3% to the neutron structure function. Hence, we expect uncertainties in our estimate of $a_{\text{SbSb}}(k)$ to have only a small effect on the other two partial structure functions derived from the two data sets through Eq. (6). The partial structure functions for liquid SbCl_3 are shown in Fig. 2. The intermolecular atom pair correlation functions obtained by Fourier transformation of the partial structure functions yield directly some valuable insight into the spatial correlations in liquid SbCl_3 , to be discussed at the end of this report.

We will now describe our attempts to compute the x-ray and neutron structure functions from statistical mechanical theory.

REFERENCE INTERACTION SITE MODELS (RISM)

The RISM theory⁹ gives site-site distribution functions for model fluids which have a site-site pair potential. This theory was used to treat SbCl_3 . The RISM equations for hard sphere interactions follow:

$$\hat{h}_{\alpha\gamma}(k) = \hat{w}_{\alpha}(k) \hat{c}_{\gamma}(k) (\mathcal{I} - \rho \hat{w}(k) \hat{c}(k))^{-1} \hat{w}_{\gamma}(k), \quad (7)$$

$$c_{\alpha\gamma}(r) = 0 \quad \text{for} \quad r > \sigma_{\alpha\gamma}, \quad (8)$$

$$h_{\alpha\gamma}(r) = -1 \quad \text{for} \quad r < \sigma_{\alpha\gamma} . \quad (9)$$

Eq. (7), which is a matrix equation, may be taken as the definition of the site-site direct correlation function matrix $\tilde{c}(k)$. Here I is the unit matrix, $\sigma_{\alpha\gamma}$ is the hard sphere diameter for the interaction between site α and site γ , and

$$\omega_{\alpha\gamma}(k) = \sin(k\ell_{\alpha\gamma})/k\ell_{\alpha\gamma} . \quad (10)$$

The quantity $\ell_{\alpha\gamma}$ is the distance between interaction site α and interaction site γ of a molecule.

For SbCl_3 an interaction site was positioned at the nucleus of each atom of the molecule. The van der Waal diameters¹⁰ of antimony and chlorine are 4.40 Å and 3.60 Å, respectively. The locations of the first peak in the experimental pair distribution functions⁴ suggest that σ_{ClCl} and σ_{SbCl} are 3.7 Å, and 3.4 Å, respectively. RISM calculations were made for values of the antimony-antimony hard sphere diameter, σ_{SbSb} , in the range 2.5 Å to 4.0 Å, and σ_{ClCl} in the range 2.8 Å to 3.6 Å with $\sigma_{\text{SbCl}} = (\sigma_{\text{SbSb}} + \sigma_{\text{ClCl}})/2$. For values of the hard sphere diameters in these ranges the magnitudes and the locations of the peaks of at least one of the RISM $H_d(k)$'s was not in agreement with the experimental results.

In this paper the best set of values for the hard sphere diameters is that which gives the $H_d(k)$'s which are in best agreement with the experimental $H_d(k)$'s. This best set was determined by a visual comparison of the RISM and experimental $H_d(k)$'s. In this determination the region of k -space in which the first peak of the $H_d(k)$'s is situated was weighed more heavily than other regions. When σ_{SbCl} is given by

$$\sigma_{\text{SbCl}} = (\sigma_{\text{SbSb}} + \sigma_{\text{ClCl}})/2 , \quad (11)$$

the best values for the hard sphere diameters are $\sigma_{\text{SbSb}} = 3.2 \text{ \AA}$, $\sigma_{\text{ClCl}} = 3.1 \text{ \AA}$, and $\sigma_{\text{SbCl}} = 3.15 \text{ \AA}$. The RISM $H_d(k)$'s for the best hard sphere diameters and the experimental $H_d(k)$'s for SbCl_3 are shown in Fig. 3. When σ_{SbCl} is given by Equation 11, the hard sphere diameters are additive. The locations of the first peak of the experimental pair distribution functions (Fig. 5) suggest that a nonadditive antimony-chlorine hard sphere diameter is suitable for SbCl_3 . However, a nonadditive σ_{SbCl} does not make the RISM results more acceptable. For example, with $\sigma_{\text{SbSb}} = 3.2 \text{ \AA}$ and $\sigma_{\text{ClCl}} = 3.1 \text{ \AA}$, the value of σ_{SbCl} was varied from $2.55 \text{ \AA}$ to $3.15 \text{ \AA}$. The best value of σ_{SbCl} in this range is the additive diameter, $3.15 \text{ \AA}$.

The RISM site-site distribution functions for $\sigma_{\text{SbSb}} = 3.2 \text{ \AA}$, $\sigma_{\text{ClCl}} = 3.1 \text{ \AA}$, and $\sigma_{\text{SbCl}} = 3.15 \text{ \AA}$ are presented in Fig. 4. Equation (2.7) of Reference 11 suggests that when a RISM molecule is a good model for a fluid, the differences between $g_{\alpha\gamma}(r)$ of the RISM theory and the experimental $g_{\alpha\gamma}(r)$ are relatively small for values of r which are not close to and which are greater than $\sigma_{\alpha\gamma}$. The disagreement between the RISM $H_d(k)$'s (Fig. 3) and site-site distribution functions (Fig. 4) and the experimental $H_d(k)$'s and pair distribution functions, Fig. 3 and 5) indicate that the best RISM molecule found is not a good model for SbCl_3 .

The last statement and the assumption that the convergence parameter, ξ , of reference 11 is small imply that the attractive region of the pair potential has a large effect on the structure of liquid SbCl_3 . The formulation of the RISM theory presented in reference 9 has been used to treat model fluids which are not based on hard sphere site-site pair potentials.¹² RISM atom pair distribution functions for Lennard-Jones site-site pair potentials for nitrogen and benzene have been obtained.

They are in good agreement with computer simulation results.^{13,14} We have also determined the RISM $H_d(k)$'s for a Lennard-Jones site-site pair potential for $SbCl_3$ with an interaction site at each nucleus. They do not differ significantly from the RISM $H_d(k)$'s of the corresponding hard sphere site-site pair potential. A pair potential with electric charges distributed on the molecule as the Ben-Naim and Stillinger effective pair potential for water¹⁵ might be a suitable pair potential for $SbCl_3$. Such pair potentials were not treated with the RISM theory, because when the charges are large enough to affect significantly the $H_d(k)$'s the RISM results appear to be inaccurate. The RISM theory seems to weigh the coulomb interactions too heavily. The last two statements are based on calculations done for an $SbCl_3$ molecule with a Buckingham potential interaction site and an electric charge on each nucleus.

DISCUSSION

Our extensive search for a RISM molecule which can predict the spatial correlations, and hence the diffraction pattern, of liquid $SbCl_3$ has been unsuccessful. We now resume our discussion of the partial structure functions (Fig. 2) derived directly from the neutron and x-ray diffraction data. The intermolecular atom pair distribution functions $g_{\alpha\gamma}(r)$ for liquid $SbCl_3$ are shown in Fig. 5 (solid lines). Also shown (dashed curves) for the average coordination numbers as computed from

$$n_{\alpha\gamma}(r) = 4\pi\rho_{\gamma} \int_0^r g_{\alpha\gamma}(r) r^2 dr . \quad (12)$$

$n_{\alpha\gamma}(r)$ is the number of γ atoms in a sphere of radius r around any origin atom α , ρ_{γ} being the bulk density of γ atoms. Defining a contact distance

$\sigma_{\alpha\gamma}$ as the smallest value of r for which $g_{\alpha\gamma}(r) = 1$, a most frequent near neighbor distance $R_{\alpha\gamma}$ as the value of r at the first maximum of $g_{\alpha\gamma}(r)$, and a first coordination sphere of radius $r_{\min}$, the value of r at the first minimum of $g_{\alpha\gamma}(r)$, we obtain the distances and coordination numbers listed in Table I.

We have already pointed out⁴ that the Sb...Cl distance (Table I) between atoms from neighboring molecules is much shorter than the distance of 4.0 Å expected from the van der Waals radii¹⁰ of Sb (2.2 Å) and Cl (1.8 Å) atoms. We now see that each Sb atom has 3 Cl neighbors from other molecules in a very well defined distribution centered around 3.40 Å, in addition to the 3 bonded Cl atoms at 2.35 Å. These numbers suggest a distorted octahedral arrangement of Cl atoms around each Sb atom in the liquid. This arrangement must be such that each Cl atom "sees" only 1 nearest Sb atom from a neighboring molecule. In the liquid each Sb atom has 2 close Sb neighbors in a sphere of radius 4.3 Å (Fig. 5), in sharp contrast to the crystal structure¹⁶ where the shortest Sb...Sb distance is 4.75 Å. The short Sb...Sb contact in liquid SbCl₃ can only be accommodated if all 3 near neighbor Cl atoms belong to one SbCl₃ molecule. If pairs of molecules are stacked like umbrellas (Fig. 6) so that all 3 intermolecular Sb...Cl distances are 3.40 Å, the Sb...Sb distance would be 3.94 Å. Whether such neighboring molecules have their Sb-Cl bonds staggered or eclipsed cannot be inferred directly from the curves in Fig. 5. However, the staggered geometry seems likely from the known preference of hexacoordinate antimony for pseudo-octahedral geometry^{17,18}. The shortest Cl...Cl distances in a pair of molecules stacked in a staggered umbrella configuration (Fig. 6) would be 4.43 Å, a distance which correlates well with the shoulder on the function $g_{\text{ClCl}}(r)$ in Fig. 5.

There are, in addition, shorter Cl...Cl contacts from other neighboring molecules at 3.85 Å. Since the corresponding Sb...Cl distances cannot be much shorter than 4.5 Å, the Cl...Cl-Sb angles in such contacts must be at least 90°, which is again in contrast with the corresponding contacts in the crystal¹⁶. A possible configuration of this type is also shown in Fig. 6.

The structure of liquid SbCl₃ just above the melting point might then be described in terms of chains of SbCl₃ molecules stacked in the umbrella configuration, with interaction between chains through van der Waals forces. The interaction between pairs of molecules within a given chain must be much stronger than these van der Waals forces, and the dipole axes of these molecules are strongly correlated, at least over one or two molecular diameters. This might explain the large dielectric constant of liquid SbCl₃.

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Table I. Contact distances $\sigma_{\alpha\gamma}$, most frequent distances $R_{\alpha\gamma}$, and average number of γ atoms in the first coordination sphere around any α atom in liquid SbCl_3 .

α	γ	$\sigma_{\alpha\gamma}$	$R_{\alpha\gamma}$	$N_{\alpha\gamma}$
Cl	Cl	3.60	3.85	8
Cl	Sb	3.20	3.40	1
Sb	Cl			3
Sb	Sb	3.35	4.00	6

CAPTIONS

- Fig. 1. Molecular scattering function $S_d^*(k)$ derived from x-ray scattering (circles) and computed angular part of the scattering $A_{NS}(k)$ (dashed curve). See text for definitions.
- Fig. 2. The k -weighted partial structure functions derived from x-ray and neutron scattering.
- Fig. 3. Distinct structure functions calculated for the "best" RISM molecule of $SbCl_3$ and derived from experiment.
- Fig. 4. Site-site distribution functions calculated for the "best" RISM molecule of $SbCl_3$.
- Fig. 5. Intermolecular atom pair distribution functions $g_{\alpha\gamma}(r)$ derived from x-ray and neutron scattering (solid lines). $n_{\alpha\gamma}(r)$ is the average number of γ atoms in a sphere of radius r around any α atom in liquid $SbCl_3$.
- Fig. 6. A typical configuration of $SbCl_3$ molecules in the liquid consistent with the experimental data. There are, of course, sizeable local and instantaneous deviations from this configuration and, hence, the correlations pictured extend only a few molecular diameters from any given origin. The spheres representing individual atoms are of arbitrary diameter, but the distances between their centers (in Å) are to scale. -

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Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6