[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

X-Ray Studies of Fused Salt Systems. III. Tin(IV) Iodide

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An analysis of the X-ray diffraction pattern of fused SnI_4 is reported. The liquid appears to consist of independent tetrahedral molecules of SnI_4 with an Sn–I distance of 2.66 Å. and an I–I distance of 4.35 Å. There is no order beyond the short range order of single molecules.

Introduction

The approximately regular tetrahedral coördination of I atoms around In atoms in fused InI_3 was reported in an earlier communication[1] from this Laboratory. The radial distribution curve for fused InI_3 showed the ratio of In–I to I–I distances to be 1.674. This ratio differs considerably from that (1.633) demanded of a regular tetrahedron, and cannot be brought to the regular value by altering the measured bond lengths within our estimated error of 0.03 Å. This circumstance led the authors to wonder whether the analytical procedure they have used, which is due to Warren, Krutter and Morningstar,[2] was indeed capable of such nicety. One way of testing the entire method (experimental plus analytical) would be to examine a substance of less equivocal structure. We have accordingly carried out an X-ray study of fused SnI_4, a substance which, from *a priori* considerations alone, almost certainly consists of individual tetrahedral molecules.

Additional correlative data are available from the structure of crystalline SnI_4 and the results of electron diffraction investigations on SnI_4 vapor. Mark and Weissenberg,[3] Ott[4] and Dickinson,[5] have described the structure of crystalline SnI_4 in terms of discrete SnI_4 molecules. The Sn–I distance is 2.64 Å., and the I–I distance is 4.32 Å. Hveding and Stromme,[6] Lister and Sutton,[7] and Hassel and Sandbo[8] are in mutual agreement on the structure of SnI_4 vapor, giving the Sn–I distance and the I–I distance as identical with the corresponding distances in the crystal. The results of the present research confirm this structure as existing in the liquid state as well.

Experimental

The SnI_4 was prepared by gentle heating of a mixture of granular tin metal and iodine crystals until the free iodine had completely evaporated. The resulting mass was cooled and extracted with CCl_4. Two recrystallizations from the same solvent yielded a yellow crystalline mass of SnI_4. The product was analyzed for Sn by conversion to SnO_2. Found: Sn, 18.57; calcd.: Sn, 18.95. This material was transferred to a Pyrex tube of 0.040 cm. inner diameter and 0.004 cm. wall thickness. The sample was melted alternately under vacuum and atmospheric pressure in order to force all the liquid into one continuous body in the bottom of the sample tube.

The experimental arrangement and procedure have been described before.[9] Crystal monochromated Mo-Kα radiation at 40 kv. and 20 ma. was allowed to irradiate the sample held at 165° for 170 hours, and the diffracted radiation recorded photographically. The diffraction photograph was microphotometered on a Leeds and Northrup recording microphotometer and film densities used as a measure of relative intensity. The raw intensity curve was corrected for film shrinkage, absorption, diffraction effects due to the container, polarization and incoherent scattering in the usual way. Figure 1 (curve C) shows the fully corrected pattern, intensity (I_{exp}) *vs.* diffraction angle. The intensity scale is absolute, the curve having been fitted to coincide at large diffraction angles with the calculated independent scattering from one Sn and four I atoms. The fitting was effected over the range of diffraction angle from 69 to 75°. The monotonic curve (B) also appearing in Fig. 1 is the independent coherent scattering, Σf_{coh}.

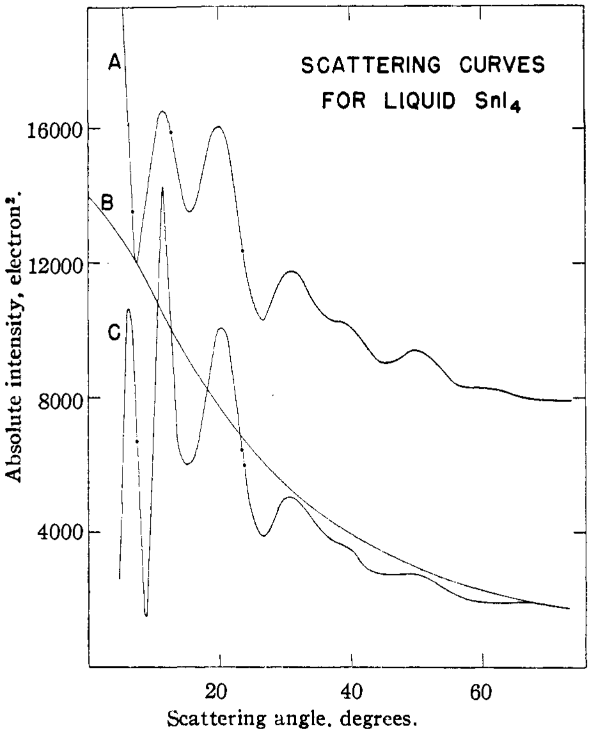

Fig. 1.—Scattering curves for liquid SnI_4: curve C is the fully corrected observed intensity; B, the calculated coherent scattering for independent atoms, Sn + 4I; A, the calculated coherent scattering for the tetrahedral assemblage, SnI_4. The ordinate for A is moved upward 6000 units.

Other publications[2,9] have described how one may proceed from the data of Figure 1 to a weighted radial distribution function. The precise physical interpretation of this function is described in the same references. James[10] has assembled an excellent exposition of the entire theory developed by Warren and his associates from an original

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[1] R. E. Wood and H. L. Ritter, THIS JOURNAL, **74**, 1760 (1952).

[2] B. E. Warren, H. Krutter and O. Morningstar, *J. Am. Ceram. Soc.*, **19**, 202 (1936).

[3] H. Mark and K. Weissenberg, *Z. physik*, **16**, 1 (1923).

[4] H. Ott, *Z. Krist.*, **63**, 222 (1926).

[5] R. G. Dickinson, *ibid.*, **64**, 400 (1927).

[6] J. A. Hveding and L. S. Stromme, *Tids. Kjemi. Bergvessen.*, **17**, 81 (1937).

[7] M. W. Lister and L. E. Sutton, *Trans. Faraday Soc.*, **37**, 393 (1941).

[8] O. Hassel and A. Sandbo, *Z. physik. Chem.*, **B41**, 75 (1938).

[9] R. L. Harris, R. E. Wood and H. L. Ritter, THIS JOURNAL, **73**, 3151 (1951).

[10] R. W. James, "The Optical Principles of the Diffraction of X-Rays," G. Bell and Sons, Ltd., London, 1948, p. 458 f.

study by Zernike and Prins. Evaluation of the radical distribution function requires a knowledge of the density of the liquid. This was measured by pycnometer and taken as 3.70 g./cc. The "effective" atomic number, K_{Sn} and K_I may be taken as the true atomic numbers.

Results and Discussions

The radial distribution function was evaluated at some 60 points. The necessary numerical integrations were carried out by means of the International Business Machines' CPC electronic computer. The radial distribution curve is shown in Fig. 2. The principal peaks occur at 2.66 and 4.35 Å. These values agree within experimental error with the Sn–I and the I–I distances found in crystalline and gaseous SnI_4. The ratio of these distances is 1.634, closer to the regular value of 1.633 than one has a right to expect.

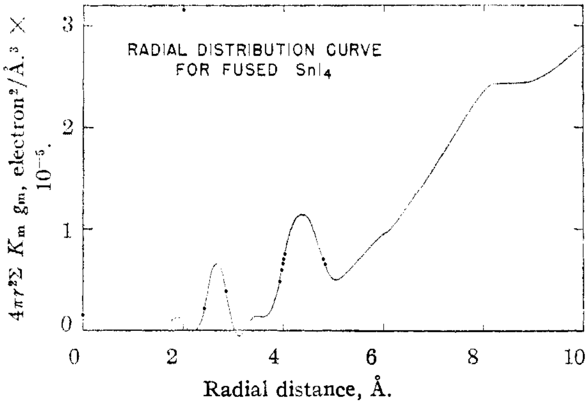

Fig. 2.—The radial distribution curve for fused SnI_4.

The area included under the first peak in Fig. 3 should equal $2nK_{Sn}K_I$, where n is the coördination number of the Sn. Taking the K's equal to the atomic numbers, and the measured area as 23800 electron², the apparent coördination number of Sn is $n = 4.55$. Previous work has shown that this number is always greater than the molecular coördination number, presumably because of intermolecular interference. It is reasonable to interpret the measured 4.55 as meaning a coördination number of 4. This value of n, together with the ratio of I–I/Sn–I, indicate almost certainly that liquid tin(IV) iodide consists of tetrahedral SnI_4 molecules.

If the second large peak is identified primarily with the I–I distance along a tetrahedral edge, interesting information is available also from the area under this peak. Let p equal the number of I atoms which lie about 4.35 Å. from one chosen I atom. The area under this peak should then be $4pK_I^2$. The measured area is 101000 electron², whence $p \sim 9.0$. Thus, instead of having only three I neighbors at this distance (as would be the case with single molecules), each I atom appears to be surrounded by 9 other I atoms at a distance of about 4.4 Å. Three of these are in the same molecule, the other six in neighboring molecules. In crystalline SnI_4, each I atom is surrounded by 12 other I atoms all at 4.32 Å. The liquid appears to be a somewhat expanded and smeared-out version of the solid, each I atom being surrounded by only 9 other approximately equidistant I atoms. The moderately large change in density (from 4.7 to 3.7 g./cc.) on melting corroborates this picture.

We are unable to account in very definite terms for the barely resolved peaks at 3.47 and about 8 Å. They are undoubtedly due to intermolecular interferences. That at 3.47 Å. is most probably the Sn–Sn distance for SnI_4 molecules in closest approach. If q represents the number of Sn atoms at this distance from any one chosen Sn atom, the area under the peak should be qK_{Sn}^2. The measured area is about 5400 electron², whence $q \sim 2.2$. This number is certainly in the right neighborhood to be consistent with the model of the liquid suggested above. The peak near 8 Å. probably has a similar significance.

No other detail is apparent in the radial distribution curve. There appears therefore to be no molecular association beyond that caused by the restricted packing due to van der Waals forces.

If there is no association, the majority of the scattering would be due to independent SnI_4 tetrahedra. The theoretical scattering produced by independent SnI_4 molecules may be calculated from the formula

$$I(s) = \sum_{i,j} f_i f_i \frac{\sin r_{ij}s}{r_{ij}s}$$

where i and j refer to the several atoms in the SnI_4 unit over which the summation is carried and r_{ij} is the distance between atoms i and j. A plot of this theoretical scattering (using the Sn–I and I–I distances derived above) is shown as curve A in Fig. 1. It will be noted that the positions of all salient features of the curve agree well with the observed scattering (curve C), except in two particulars: the appearance of an innermost peak and the outward shifting of the outermost peak in the observed curve. The innermost observed peak appears in all liquid patterns and is an intermolecular interference assumed absent in the theoretical calculation. The corresponding Bragg d is about 7–8 Å. The shifting of the outermost peak is another manifestation of the conclusion already reached that interferences in the region of low r are partially intramolecular.

Acknowledgment.—The authors wish to express their appreciation to the Wisconsin Alumni Research Foundation and to the du Pont Company for grants-in-aid which made this work possible. We wish also to record our indebtedness to K. J. Arnold and W. E. Johnson of the Computing Service, Department of Mathematics, University of Wisconsin, for devising the IBM computational procedure; and to F. P. Hochgesang of the Socony-Vacuum Oil Company for his help in microphotometering our films.

MADISON, WISCONSIN RECEIVED JULY 23, 1951