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## The Structure of 2-Methyl-2-propanol at 293 K

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### Abstract

The angular distributions of the scattered X-ray intensity from 2-methyl-2-propanol in the liquid phase were measured with Cu  $K\alpha$  and Mo  $K\alpha$  radiation lines. From these an experimental pair-function distribution was calculated. This is compared with the pair-function distributions from several models. Good agreement is obtained for two types of association. The first is a dimer with an open hydrogen-bond structure. The second is a cyclic trimer. The average length of the hydrogen bond in the dimers and the trimers is 3.08 and 2.46 Å, respectively. Association involving more than three molecules having the chain or cyclic structure is excluded.

### Introduction

The association of 2-methyl-2-propanol in the liquid state has been investigated by Liddel & Becker (1957), who assumed dimers with a cyclic structure only, and by Bellamy & Pace (1966) and by Korppi-Tommola (1977), who assumed an open structure.

The coexistence of dimers with higher polymers is favoured by Davis, Pitzer & Rao (1960) and Van Ness,

Van Winkle, Richtol & Hollinger (1967). Saunders & Hyne (1958), Huyskens, Henry & Gillerot (1962) and Storek & Kriegsmann (1968) exclude the dimers and suggest the occurrence of trimers only. Tucker, Farnham & Christian (1969) and Tucker & Becker (1973) assume the coexistence of trimers and higher polymers.

X-ray diffraction studies were undertaken by Narten & Sandler (1979), who have determined the hydrogen-bond length from the maximum in the intermolecular radial-distribution function. This paper is a determination of a structural model of 2-methyl-2-propanol using the pair-function method, which permits a more exact interpretation of the X-ray diffraction data.

### Experimental

The sample obtained from recrystallization of analytically pure 2-methyl-2-propanol was measured at  $293 \pm 0.2$  K in a thermostated cuvette 1 mm thick with mica windows. The intensity of the scattered beam was measured between  $s_0 = 4\pi \sin \theta_0 / \lambda = 0.300 \text{ \AA}^{-1}$  and  $s_m = 11.831 \text{ \AA}^{-1}$  using Cu  $K\alpha$  ( $\lambda = 1.5418 \text{ \AA}$ ) and Mo  $K\alpha$  ( $\lambda = 0.7107 \text{ \AA}$ ) radiations. A transmission arrangement has been used with a flat-crystal mono-

chromator inserted in the primary beam. Corrections for background, polarization, absorption and Compton scattering were made to the angular distribution of the scattered-radiation intensity averaged from several independent measurements. The average angular distribution was normalized by Norman's method (1957).

The interpretation of the experimental results was performed by the method of the pair-function distribution calculated from the equation (Warren, 1969):

$$\sum_{uc} \sum_i \frac{N_{ij}}{R_{ij}} P_{ij}(R) = 2\pi^2 R \rho_e \sum_{uc} Z_j + \int_0^{s_m} si(s) \times \exp(-\alpha^2 s^2) \sin(sR) ds, \quad (1)$$

where:  $\sum_{uc}$  is over a unit of composition,  $N_{ij}$  is the average number of neighbours in the  $i$ th shell around atom  $j$  at a distance  $R_{ij}$ ,  $P_{ij}$  is the pair function,  $\rho_e$  is the average electron density,  $Z_j$  the number of electrons in the  $j$ th atom,  $s = 4\pi \sin \theta / \lambda$ ,  $i(s) = [I_{eu}/N - \sum_{uc} f_j^2] / g^2(s)$ , is the structural-sensitive part of the total coherent intensity  $I_{eu}/N$  in electron units per molecule,  $g(s) = \sum_{uc} f_j / \sum_{uc} Z_j$  is a sharpening factor,  $\exp(-\alpha^2 s^2)$  is a convergence factor.

The pair functions  $P_{ij}(R)$  for particular interatomic interactions are calculated from the following relation:

$$P_{ij}(R) = \int_0^{s_m} [f_i f_j / g^2(s)] \exp(-\alpha^2 s^2) \sin(sR_{ij}) \times \sin(sR) ds. \quad (2)$$

When calculating the  $P_{ij}(R)$  function, the auxiliary pair function was applied:

$$Q_{ij}(x) = \frac{1}{2} \int_0^{s_m} [f_i f_j / g^2(s)] \exp(-\alpha^2 s^2) \cos(xs) ds. \quad (3)$$

The interrelation between  $Q_{ij}(x)$  and  $P_{ij}(R)$  is as follows:

$$P_{ij}(R) = Q_{ij}(R - R_{ij}) - Q_{ij}(R + R_{ij}). \quad (4)$$

The method consists in finding a set of pair functions defined by the left side of equation (1) which would give the curve described by the right side of equation (1) determined from the experimental measurements. The values of the  $s_m$  and  $\alpha$  factors applied in the calculations of both experimental and theoretical pair functions must be the same.

The maximum error of the experimental pair-function distribution curve was estimated not to exceed 5%.

### The results and interpretation

The intensity curves  $I_{eu}/N$  in electron units per unit of composition obtained from Cu  $K\alpha$  and Mo  $K\alpha$  measurements are shown by Fig. 1.

The integrand of equation (1),  $si(s) \exp(-\alpha^2 s^2)$ , with coefficient  $\alpha = 0.06$ , is shown as curve *A* of Fig. 2. Curve *B* of Fig. 2 shows the theoretical curve  $si_m(s)$  calculated from the equation (Debye, 1941):

$$i_m(s) = \left[ \sum_{i \neq j} f_i f_j \exp(-l_{ij}^2 s^2 / 2) \sin(sR_{ij}) \right] \left[ \sum_i f_i(s) \right]^{-2} \quad (5)$$

Molecular parameters  $R_{ij}$  (Table 1) have been fitted by a testing method (Narten, 1979) assuming that  $i(s) \approx i_m(s)$  for high values of  $s$  ( $s \gtrsim 8 \text{ \AA}^{-1}$ ).

Fig. 3 shows the experimental and theoretical pair-function distributions. The theoretical curve is a sum of curves calculated for intramolecular (curve 1) and intermolecular (curve 2) interactions. Both curves were obtained from the function  $Q_{ij}(x)$  (Fig. 4a) calculated for the combination of atom pairs and groups of atoms in 2-methyl-2-propanol.

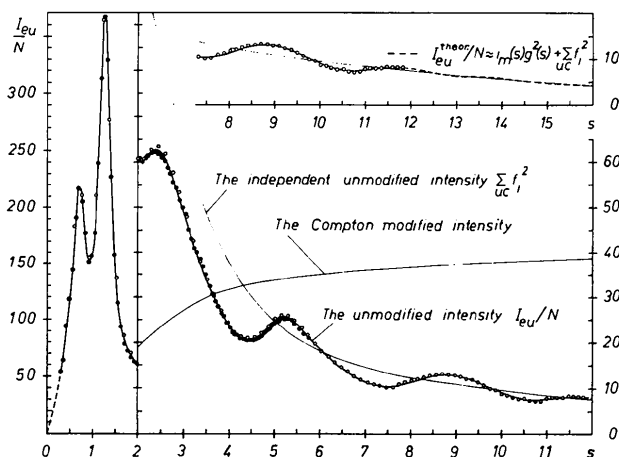


Fig. 1. Measured intensity curve for 2-methyl-2-propanol with Cu  $K\alpha$  (filled circles) and Mo  $K\alpha$  (open circles).

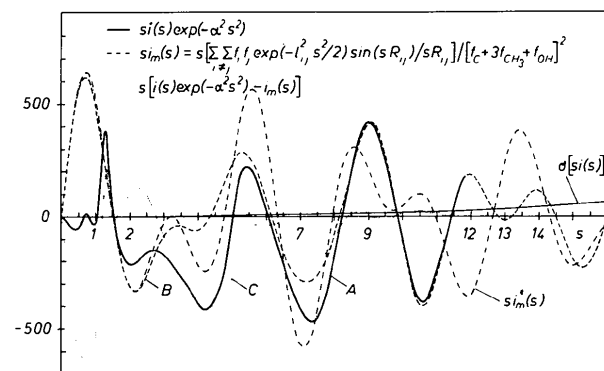


Fig. 2. Curve *A* (continuous line), the experimental structure function  $si(s) \exp(-\alpha^2 s^2)$ . Curve *B* (broken line), the molecular structure function  $si_m(s)$  calculated according to Debye (1941). Curve *C* (dotted line), subtraction of the calculated curve *B* from the curve *A*. Curve  $\sigma[si(s)]$  represents the standard deviations of the total structure function  $si(s) \exp(-\alpha^2 s^2)$  calculated according to Konnert & Karle (1973).

Table 1. Types of intramolecular interactions and the  $\sum_{uc} \sum_i N_{ij}/R_{ij}$  values for 2-methyl-2-propanol

Type of intramolecular interactions	This work	Narten & Sandler (1979)
C(1)-O	2/1.48	2/1.43
C(1)-C(2), C(1)-C(3), C(1)-C(4)	6/1.62	6/1.54
C(2)-O, C(3)-O, C(4)-O	6/2.30	6/2.42
C(2)-C(3), C(3)-C(4), C(4)-C(2)	6/2.79	6/2.51

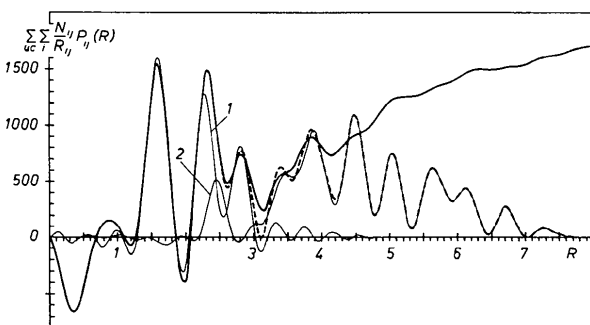


Fig. 3. Comparison of the theoretically calculated pair function (broken line) and the experimental curve (continuous line) obtained for 2-methyl-2-propanol. Curve 1, calculated for the intramolecular interactions. Curve 2, calculated for the intermolecular interactions.

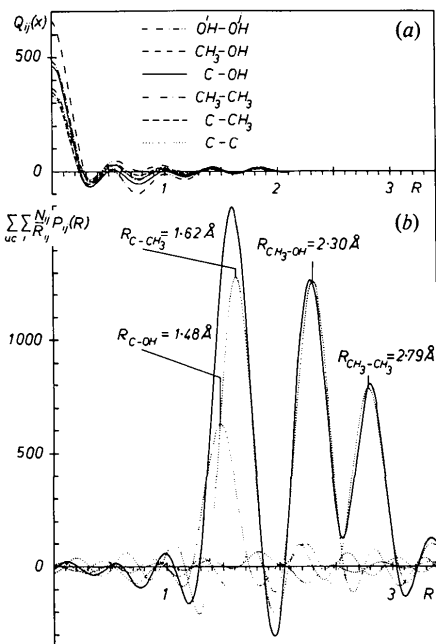


Fig. 4. The pair function for 2-methyl-2-propanol. (a)  $Q_{ij}(x)$  function for the interatomic interactions in 2-methyl-2-propanol. (b) Theoretical curve of the pair function for intramolecular interactions (continuous line) and discrete maxima for individual intramolecular interactions (dotted lines).

Atomic scattering factors  $f_C$ ,  $f_{CH_3}$  and  $f_{OH}$  were calculated according to the formula (*International Tables for X-ray Crystallography*, 1974):

$$f(\lambda^{-1} \sin \theta) = \sum_{i=1}^4 a_i \exp(-b_i \lambda^{-2} \sin^2 \theta) + C \quad (6)$$

using the  $a_i$ ,  $b_i$  and  $C$  values determined by Narten (1979).

The fit of the theoretical curve of the pair-function distribution to the experimental curve was performed for two coefficients  $\alpha$  (0.03 and 0.06) and for several values of  $s_m$  (11.365, 11.831, 12.502, 13.544, 14.483, 15.312 and 16.000  $\text{\AA}^{-1}$ ). For the values of  $s > 11.831 \text{\AA}^{-1}$  the experimental data of curve  $si(s) \times \exp(-\alpha^2 s^2)$  (curve A in Fig. 2) were complemented with the theoretical data of curve  $si_m(s)$  (curve B in Fig. 2). The best fit between the theoretical and experimental

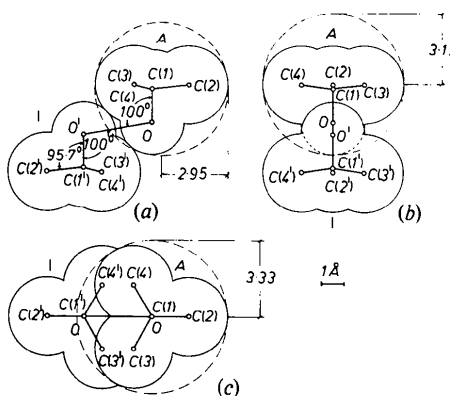


Fig. 5. The model of the dimer of 2-methyl-2-propanol. (a) Orthogonal projection of the model onto the plane of the O-C(1) and C(1)-C(2) bonds. (b) Orthogonal projection of the model onto the plane perpendicular to the plane of the O and C(1) atoms. (c) Orthogonal projection of the model onto the plane perpendicular to the directions of the O-C(1) bonds.

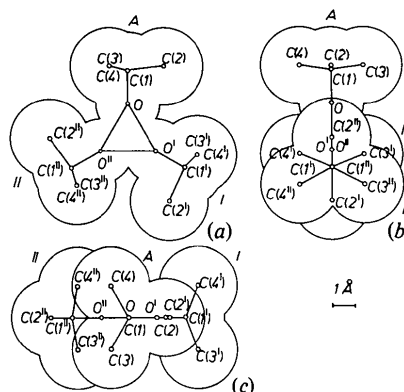


Fig. 6. Model of the trimer of 2-methyl-2-propanol. (a) Orthogonal projection of the model onto the plane of the O-C(1) and C(1)-C(2) bonds. (b) Orthogonal projection of the model onto the plane perpendicular to the plane of the O and C(1) atoms. (c) Orthogonal projection of the model onto the plane perpendicular to the directions of the O-C(1) bonds.

pair functions is obtained for  $\alpha = 0.06$  and  $s_m = 11.831 \text{ \AA}^{-1}$  and for the intramolecular distances  $R_{ij}$  given in Fig. 4(b). The same parameters  $R_{ij}$  were determined by the fit of the termination of the theoretical curve *B* (Fig. 2) to the experimental curve *A* (Table 1). Table 1 gives the values of  $\sum_{uc} \sum_i N_{ij}/R_{ij}$  for intramolecular interactions in the 2-methyl-2-propanol molecule.

The atomic notation used in Table 1 is shown in Fig. 5. The experimental curve of the pair-function distribution shown in Fig. 3 was interpreted by various models of the associates of 2-methyl-2-propanol. The

Table 2. Types of intermolecular interactions and the  $\sum_{uc} \sum_i N_{ij}/R_{ij}$  values for the assumed 2-methyl-2-propanol structure model

Type of intermolecular interactions	Peak no.	$\sum_{uc} \sum_i N_{ij}/R_{ij}$
For the dimer structure model		
O—O <sup>I</sup>	—	1/3.08
O—C(3 <sup>I</sup> ), O—C(4 <sup>I</sup> ), C(3)—O <sup>I</sup> , C(4)—O <sup>I</sup>	1	4/3.40
O—C(1 <sup>I</sup> ), C(1)—O <sup>I</sup>	2	2/3.64
C(3)—C(3 <sup>I</sup> ), C(4)—C(4 <sup>I</sup> )	3	2/4.05
C(1)—C(3 <sup>I</sup> ), C(1)—C(4 <sup>I</sup> ), C(3)—C(1 <sup>I</sup> ), C(4)—C(1 <sup>I</sup> )	4	4/4.45
C(1)—C(1 <sup>I</sup> )	5	1/4.62
C(3)—C(4 <sup>I</sup> ), C(4)—C(3 <sup>I</sup> )	6	2/4.95
O—C(2 <sup>I</sup> ), C(2)—O <sup>I</sup>	7	2/5.12
C(2)—C(3 <sup>I</sup> ), C(2)—C(4 <sup>I</sup> ), C(3)—C(2 <sup>I</sup> ), C(4)—C(2 <sup>I</sup> )	8	4/5.65
C(1)—C(2 <sup>I</sup> ), C(2)—C(1 <sup>I</sup> )	9	2/5.90
C(2)—C(2 <sup>I</sup> )	10	1/7.33
For the trimer structure model		
O—O <sup>I</sup> , O—O <sup>II</sup>	—	2/2.46
O—C(2 <sup>II</sup> ), C(2)—O <sup>I</sup>	1	2/3.79
O—C(1 <sup>I</sup> ), C(1)—O <sup>I</sup> , O—C(1 <sup>II</sup> ), C(1)—O <sup>II</sup>	2	4/3.81
O—C(3 <sup>I</sup> ), O—C(4 <sup>I</sup> ), C(3)—O <sup>II</sup> , C(4)—O <sup>II</sup>	3	4/4.05
C(2)—C(3 <sup>I</sup> ), C(2)—C(4 <sup>I</sup> ), C(3)—C(2 <sup>II</sup> ), C(4)—C(2 <sup>II</sup> )	4	4/4.37
O—C(3 <sup>II</sup> ), O—C(4 <sup>II</sup> ), C(3)—O <sup>I</sup> , C(4)—O <sup>I</sup>	5	4/4.50
C(1)—C(2 <sup>II</sup> ), C(2)—C(1 <sup>I</sup> )	6	2/4.59
O—C(2 <sup>I</sup> ), C(2)—O <sup>II</sup>	7	2/4.72
C(1)—C(1 <sup>I</sup> ), C(1)—C(1 <sup>II</sup> )	8	2/5.02
C(1)—C(3 <sup>I</sup> ), C(1)—C(4 <sup>I</sup> ), C(3)—C(1 <sup>II</sup> ), C(4)—C(1 <sup>II</sup> )	9	4/5.05
C(3)—C(3 <sup>I</sup> ), C(4)—C(4 <sup>I</sup> ), C(3)—C(3 <sup>II</sup> ), C(4)—C(4 <sup>II</sup> )	10	4/5.50
C(3)—C(1 <sup>I</sup> ), C(4)—C(1 <sup>I</sup> ), C(1)—C(3 <sup>II</sup> ), C(1)—C(4 <sup>II</sup> )	11	4/5.75
C(2)—C(2 <sup>I</sup> ), C(2)—C(2 <sup>II</sup> )	12	2/5.99
C(1)—C(2 <sup>I</sup> ), C(2)—C(1 <sup>II</sup> )	13	2/6.11
C(3)—C(4 <sup>I</sup> ), C(4)—C(3 <sup>I</sup> ), C(3)—C(4 <sup>II</sup> ), C(4)—C(3 <sup>II</sup> )	14	4/6.20
C(3)—C(2 <sup>I</sup> ), C(4)—C(2 <sup>I</sup> ), C(2)—C(3 <sup>II</sup> ), C(2)—C(4 <sup>II</sup> )	15	4/6.70

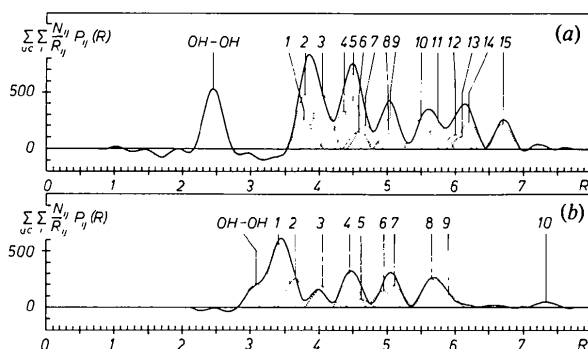


Fig. 7. Pair-function distribution curves theoretically obtained: (a) for the model of the trimer of 2-methyl-2-propanol, (b) for the model of the dimer of 2-methyl-2-propanol.

association models with open- and closed-chain structures were considered. The following were taken as the variables: (1) the number of associated molecules, (2) the hydrogen-bond lengths, (3) the angle between the hydrogen bonds and (4) the spatial arrangement of molecules. The proposed models of the association of 2-methyl-2-propanol are given in Figs. 5 and 6.

Table 2 gives the values of  $\sum_{uc} \sum_i N_{ij}/R_{ij}$  for the interatomic interactions of the proposed models of 2-methyl-2-propanol. Theoretical pair-function distributions for the models proposed are given in Fig. 7. In Fig. 7 and in Table 2 the intermolecular interactions are denoted by Arabic numerals. The termination satellites of the discrete maxima are not included in Fig. 7.

## Discussion

Assuming equal probability of dimers and cyclic trimers the corresponding pair functions were combined giving the curve 2 in Fig. 3. The curve 2 combined with the curve 1, which describes the intramolecular interactions, gives a good agreement with the experimental curve. Above 4 Å (Fig. 3) the theoretical curve is lower than the experimental because the theoretical pair function includes only the contributions from the interaction of pairs within the range of the models proposed (Table 2). The remainder of the environment is not taken into account. The maxima in the theoretical curve are more pronounced than the corresponding maxima in the experimental curve. This arises from the thermal libration and translation of the molecules and, to a lesser degree, from the internal vibration of the atoms. All the models considered are rejected except the open dimer and cyclic trimer, on the basis of a comparison between the calculated curves and the experimental curve of the pair-function distribution. For the three structural models chosen these comparisons are shown in Fig. 8. Curve 1 is obtained for a polymer with a hydrogen-bond length of 2.46 Å and an angle between the bonds OH...O equal to 105°. The pair-function distribution for the cyclic trimer with  $R_{OH...OH} = 2.46 \text{ \AA}$  (Fig. 7a), connected with that for the cyclic tetramer for which  $R_{OH...OH} = 3.08 \text{ \AA}$ , is shown as curve 2 in Fig. 8. Curve 3 illustrates the pair-function distribution for the dimer with  $R_{OH...OH} = 2.46 \text{ \AA}$  and an angle between C—OH and OH...O bonds of 120°, connected with that for the cyclic tetramer with  $R_{OH...OH} = 3.08 \text{ \AA}$ . Curves 2 and 3 were constructed assuming equal probability of trimer and dimer, and dimer and tetramer respectively.

The pair functions 1, 2 and 3 presented in Fig. 8 favour OH...OH distances of 2.46 and 3.08 Å. These values allow one to find the fit between the theoretical and experimental curves, especially for  $R < 3.4 \text{ \AA}$  where the main contribution is due to intramolecular interactions. However, for  $R > 3 \text{ \AA}$  the course of functions 1, 2 and 3 (Fig. 8) differs considerably from

the experimental curve. Therefore the structural models presented in Fig. 8 were rejected together with other models of the considered polymer with different OH...OH distances and various molecular configurations. The maximum of the functions 1 in Fig. 8 obtained for  $3 \text{ \AA} < R < 4 \text{ \AA}$  is several times greater than the maximum on the experimental curve.

The validity of the above conclusions depends on the data accuracy and on the range of  $s = 4\pi \sin \theta / \lambda$ . In this work  $I(s)$  values were measured for  $0.300 \text{ \AA}^{-1} \leq s \leq 5.763 \text{ \AA}^{-1}$  and  $0.617 \text{ \AA}^{-1} \leq s \leq 11.831 \text{ \AA}^{-1}$  with Cu  $K\alpha$  and Mo  $K\alpha$  radiations, respectively. Only the data obtained for  $s_m \leq 11.831 \text{ \AA}^{-1}$  were considered in order to eliminate the influence of spurious waves of the  $I(s)$  curve for higher values of  $s$  on the final course of the pair function. The spurious waves of the  $I(s)$  curve result from high Compton scattering, which is a few times greater than the unmodified intensity  $I_{eu}/N$  (Fig. 1). This effect prevents the correct evaluation of the experimental  $I(s)$  data for  $s > 12 \text{ \AA}^{-1}$  [see Hajdu, Lengyel & Pálkás (1976) and Skryshevskii (1980)]. In this work the experimental data  $si(s) \exp(-\alpha^2 s^2)$  (Fig. 2, curve A) were complemented with theoretical data of the curve  $i_m(s)$  (Fig. 2, curve B) to the  $s_m$  value equal to  $16 \text{ \AA}^{-1}$ . Therefore the fitting process of the theoretical pair-function distributions to the experimental one could be done over a wider range of  $s_m$  values. The above procedure did not influence the course of the experimental pair function and its interpretation. Detailed analysis of the results obtained proved that a fit between the theoretical and experimental curves is possible for  $\alpha = 0.06$  and for  $s_m$  values ranging from  $s_m = 11.831$  to  $14.483 \text{ \AA}^{-1}$ .

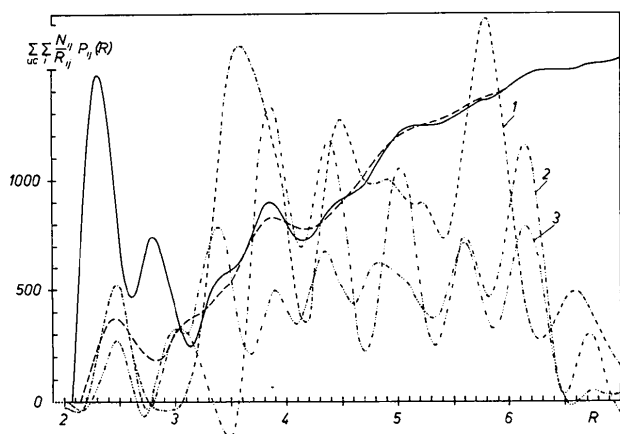


Fig. 8. Pair-function distributions for 2-methyl-2-propanol: continuous line, the experimental pair-function distribution curve; broken line, the intermolecular pair-function distribution curve; curves 1–3, theoretically calculated intermolecular pair functions: curve 1, for the polymer with  $R_{OH...OH} = 2.46 \text{ \AA}$  and an angle between OH...O bonds of  $105^\circ$ ; curve 2, for the cyclic trimer with  $R_{OH...OH} = 2.46 \text{ \AA}$  and cyclic tetramer with  $R_{OH...OH} = 3.08 \text{ \AA}$ ; curve 3, for the dimer with  $R_{OH...OH} = 2.46 \text{ \AA}$  and an angle between C–OH and OH...O bonds of  $120^\circ$  and for the cyclic tetramer with  $R_{OH...OH} = 3.08 \text{ \AA}$ .

The validity of the self-association model of 2-methyl-2-propanol assumed in this paper is confirmed by the positions of the maxima in the intermolecular pair function (Fig. 8, broken line) which was calculated from the  $s[i(s) \exp(-\alpha^2 s^2) - i_m(s)]$  function (Fig. 2, curve C).

### Comparison with other measurements

Fig. 9 presents a comparison between the experimental curves  $I_{eu}/N \equiv S(k)$  obtained in this work and by Narten & Sandler (1979), and between the curves  $I(\theta)$  obtained in this work and by Korsunskii, Yuriev & Nabierukhin (1976).

The amplitudes of the first two maxima for  $s = 0.72$  and  $1.28 \text{ \AA}^{-1}$  (this work) and for  $s = 0.77$  and  $1.33 \text{ \AA}^{-1}$  (Narten & Sandler, 1979) are found to be significantly different. On the other hand, the  $I(\theta)$  function obtained in this paper and by Korsunskii *et al.* (1976) are satisfactorily consistent.

Generally, the course of  $I_{eu}/N$  for  $s \leq 8 \text{ \AA}^{-1}$  is qualitatively consistent with the curve presented by Narten & Sandler (1979). Although for  $s \geq 8 \text{ \AA}^{-1}$  both curves approach the curve  $\sum_{uc} f_i^2$  [Fig. 1 (this work) and Fig. 1 (Narten & Sandler, 1979)], deviations are found in the terminal oscillations which determine the values of the  $R_{ij}$  parameters. Fig. 2 includes the function  $si_m^*(s) \equiv kH_m(k)$  calculated for  $R_{ij}$  parameters (Table 1) given by Narten & Sandler (1979).

The most probable cause of the observed discrepancies between the experimental curves obtained by different authors (Fig. 9) is the difficulty in properly adjusting the amplifier in the measuring setup to obtain both very low and very high values of the intensity  $I(\theta)$ .

The author thanks Professor Marian Surma for his kind interest and stimulating discussions.

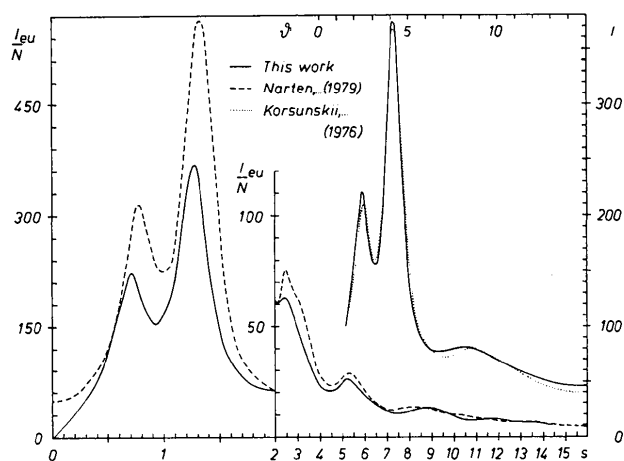


Fig. 9. A comparison between the experimental curves of intensity obtained for 2-methyl-2-propanol by various authors.

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*Acta Cryst.* (1983). **B39**, 399

**Atom distributions in sigma phases. II. Erratum.** By H. L. YAKEL, *Metals and Ceramics Division, Oak Ridge National Laboratory, PO Box X, Oak Ridge, Tennessee 37830, USA*

(Received 14 February 1983)

## Abstract

A printer's error is corrected. In Fig. 2 of the paper by Yakel [*Acta Cryst.* (1983), **B39**, 28–33] the lowest of the three bar  
0108-7681/83/030399-01\$01.50

graphs shown for the iron distributions should be diagonally lined to match the description in the figure legend.

The *Abstract* contains all relevant details.

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## Book Reviews

*Works intended for notice in this column should be sent direct to the Book-Review Editor (J. H. Robertson, School of Chemistry, University of Leeds, Leeds LS2 9JT, England). As far as practicable books will be reviewed in a country different from that of publication.*

*Acta Cryst.* (1983). **B39**, 399–400

**Geometrical and structural crystallography.** By J. V. SMITH. Pp. xiii + 450. London: John Wiley, 1982. Price £18.75.

I enjoyed this book; insofar as the author ends his preface with the words 'Enjoy yourself too', he has plainly succeeded in his aims in respect of at least one reader. It is a beautifully produced, well written and clearly illustrated account of classical crystallography of the sort normally associated with mineralogy courses. The treatment of the topics covered is

thorough, and a particularly appealing feature is the inclusion of copious exercises at the end of each chapter.

The book begins with a treatment of packing considerations, and from this develops the ideas of pattern, unit cell and crystal shape and symmetry, introducing in two dimensions concepts later treated more fully in three. Polyhedra and crystal drawing are thoroughly and clearly treated, and finally the reader is gently led towards a full discussion of space-group considerations. At each stage the concepts are illustrated by reference to real structures (generally of mineralogical significance) and the author is always careful to introduce the relevant physical picture before filling in the mathematical background.