Bull. Chem. Soc. Jpn., 57, 644—647 (1984)

The Structure of Liquid Alcohols by Neutron Diffraction. I. Molecular Structure of Methyl Alcohol

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(Received June 25, 1983)

The structure factor $S_m(Q)$ for liquid methyl alcohol (CD_3OD) at room temperature was obtained by means of the LINAC-TOF neutron diffraction method. An analysis of the diffraction data was carried out, and the molecular structure of CD_3OD in liquid phase was determined as: the O-D, C-O, and C-D bond lengths are 0.990±0.010, 1.435±0.005, and 1.085±0.005 Å, respectively. The O-D and C-D lengths were found to be longer than those values determined in gaseous phase.

The usefulness of the LINAC-TOF neutron diffraction method for the structure analysis of liquid systems has recently become progressively evident. Its merit in comparison with usual X-ray analysis is especially clear for the structure analysis of liquids composed of molecules including hydrogen atoms. In the preceding papers,[1,2] the structure of liquid water (D_2O) was determined to contain hydrogen-bonded tetrahedral pentamers as a main constituent. Here we extend our study of liquid structures to the next example of hydrogen-bonded liquids, *i.e.*, liquid methyl alcohol. Then, the present study aims first to determine the structure of methyl alcohol molecules in liquid phase.

By using microwave[3—5] and electron diffraction techniques,[6] several authors have performed studies of gaseous methyl alcohol and its molecular geometry in gaseous phase has been elucidated. However, studies of the molecular structure in its liquid phase are very few. From a great deal of spectroscopic data, the hydroxyl groups in liquid methyl alcohol are known to be concerned with hydrogen bonding.[7,8] The molecules are supposed to make up an aggregate by hydrogen bonding in the liquid. It is expected, for example, that, as well as in the case of water, the O-H bond length of methyl alcohol molecules is strongly influenced by the existence of hydrogen bonding in the liquid phase. Thus, the determination of the molecular geometry of liquid methyl alcohol is required as the starting point of a detailed investigation of its properties, and also the variation in the molecular structure from gaseous to liquid phases is very interesting.

Recently, Montague *et al.*[9] performed a neutron diffraction study of liquid CD_3OD by means of the reactor conventional method. However, as described in later sections, their results are considered to contain important implausible aspects, showing the restriction in the conventional method. Then, we have carried out a LINAC-TOF neutron diffraction measurement on methyl alcohol and have made an analysis of the data to determine its molecular structure.

Experimental

The experiment was performed by means of the TOF neutron diffraction method, using pulsed neutrons produced by electron LINAC at Hokkaido University. As the sample, deuterated methyl alcohol CD_3OD (purity of deuteration 99.5%, Commisariat à l'Energie Atomique (CEA), France) was used. Measurements were carried out at room temperature at five different scattering angles: $2\theta=32.0°$, 42.0°, 66.5°, and 90.5° at 10.0±0.5 °C, and, $2\theta=140.7°$ at 16.5±0.5°C.

Corrections for background, absorption, multiple scattering, inelastic scattering, and incoherent scattering were performed in the usual manner.[2,10,11] Absolute normalization of data was carried out by using the scattering data from a polycrystalline vanadium rod as an isotropic and incoherent scatterer. The structure factors $S_m(Q)$ thus determined after all corrections and calibrations of Q-scale are shown in Fig. 1 for five scattering angles. The coincidence of the values from different angles in each overlapping region of Q is quite well as seen in Fig. 1, and, combining these data sets, we obtained the final $S_m(Q)$ values of wide Q range as given in Table 1. The statistical error for values of the $S_m(Q)$ is smaller than 1.0%, and the resolving power $\Delta Q/Q$ less than a few % in the whole range of Q.[11]

Procedures of Analysis

The structure factor $S_m(Q)$ for molecular liquids consists of an intramolecular structure factor $f_1(Q)$ and

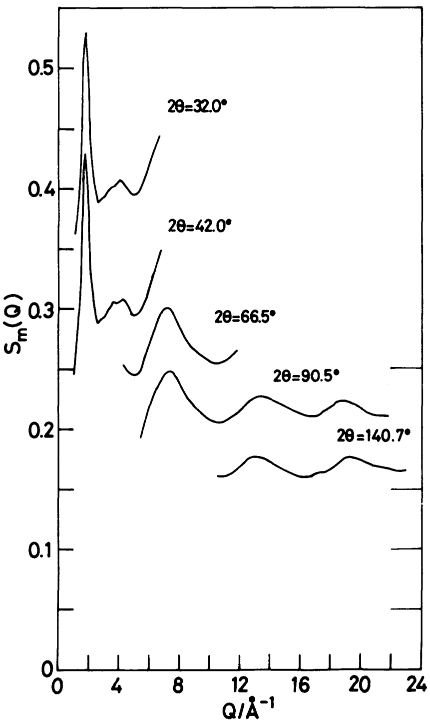

Fig. 1. Observed neutron structure factors $S_m(Q)$ for deuterated methyl alcohol at various scattering angles.

Table 1. The observed absolute neutron scattering factor $S_m(Q)$ as a function of scattering vector $Q/\text{Å}^{-1}$ for deuterated methyl alcohol

$Q/\text{Å}^{-1}$	$S_m(Q)$	$Q/\text{Å}^{-1}$	$S_m(Q)$	$Q/\text{Å}^{-1}$	$S_m(Q)$	$Q/\text{Å}^{-1}$	$S_m(Q)$
1.00	0.113	4.90	0.144	10.00	0.156	15.10	0.166
1.05	0.113	5.00	0.145	10.10	0.155	15.20	0.166
1.10	0.114	5.10	0.145	10.20	0.155	15.30	0.165
1.15	0.116	5.20	0.146	10.30	0.154	15.40	0.164
1.20	0.126	5.30	0.147	10.40	0.154	15.50	0.164
1.25	0.132	5.40	0.149	10.50	0.154	15.60	0.163
1.30	0.144	5.50	0.151	10.60	0.154	15.70	0.163
1.35	0.155	5.60	0.152	10.70	0.154	15.80	0.162
1.40	0.170	5.70	0.155	10.80	0.155	15.90	0.161
1.45	0.189	5.80	0.159	10.90	0.155	16.00	0.161
1.50	0.210	5.90	0.163	11.00	0.156	16.10	0.161
1.55	0.224	6.00	0.167	11.10	0.157	16.20	0.161
1.60	0.244	6.10	0.171	11.20	0.157	16.30	0.161
1.65	0.262	6.20	0.176	11.30	0.158	16.40	0.161
1.70	0.271	6.30	0.181	11.40	0.158	16.50	0.160
1.75	0.274	6.40	0.186	11.50	0.159	16.60	0.160
1.80	0.271	6.50	0.189	11.60	0.160	16.70	0.160
1.85	0.259	6.60	0.192	11.70	0.161	16.80	0.159
1.90	0.245	6.70	0.195	11.80	0.162	16.90	0.159
1.95	0.230	6.80	0.196	11.90	0.163	17.00	0.158
2.00	0.213	6.90	0.197	12.00	0.164	17.10	0.159
2.05	0.199	7.00	0.199	12.10	0.166	17.20	0.160
2.10	0.186	7.10	0.199	12.20	0.167	17.30	0.161
2.15	0.169	7.20	0.199	12.30	0.168	17.40	0.162
2.20	0.159	7.30	0.198	12.40	0.170	17.50	0.163
2.30	0.147	7.40	0.196	12.50	0.171	17.60	0.164
2.40	0.141	7.50	0.195	12.60	0.172	17.70	0.164
2.50	0.140	7.60	0.193	12.70	0.173	17.80	0.164
2.60	0.138	7.70	0.191	12.80	0.174	17.90	0.165
2.70	0.139	7.80	0.189	12.90	0.174	18.00	0.166
2.80	0.141	7.90	0.186	13.00	0.175	18.10	0.167
2.90	0.142	8.00	0.183	13.10	0.175	18.20	0.168
3.00	0.142	8.10	0.181	13.20	0.176	18.30	0.169
3.10	0.144	8.20	0.178	13.30	0.176	18.40	0.169
3.20	0.146	8.30	0.176	13.40	0.176	18.50	0.171
3.30	0.149	8.40	0.174	13.50	0.176	18.60	0.172
3.40	0.151	8.50	0.172	13.60	0.175	18.70	0.174
3.50	0.154	8.60	0.170	13.70	0.175	18.80	0.175
3.60	0.154	8.70	0.168	13.80	0.175	18.90	0.175
3.70	0.154	8.80	0.167	13.90	0.174	19.00	0.175
3.80	0.153	8.90	0.166	14.00	0.174	19.10	0.176
3.90	0.154	9.00	0.165	14.10	0.173	19.20	0.175
4.00	0.155	9.10	0.164	14.20	0.173	19.30	0.174
4.10	0.157	9.20	0.163	14.30	0.172	19.40	0.174
4.20	0.157	9.30	0.162	14.40	0.172	19.50	0.173
4.30	0.156	9.40	0.161	14.50	0.170	19.60	0.172
4.40	0.154	9.50	0.160	14.60	0.169	19.70	0.171
4.50	0.152	9.60	0.159	14.70	0.168	19.80	0.170
4.60	0.150	9.70	0.158	14.80	0.168	19.90	0.169
4.70	0.147	9.80	0.158	14.90	0.167	20.00	0.168
4.80	0.146	9.90	0.157	15.00	0.167		

intermolecular one. The $S_m(Q)$ for a higher Q region is characteristic of the intramolecular structure ($S_m(Q) \rightarrow f_1(Q)$ for high Q). The $f_1(Q)$ is written as

$$f_1(Q) = (\sum_i b_i)^{-2}\sum_{ij} b_i b_j j_0(Q r_{ij})\exp(-\gamma_{ij}Q^2), \qquad (1)$$

where b_i is the coherent scattering length of i-th nucleus in the molecule, r_{ij} the distance between i-th and j-th nucleus, $2\gamma_{ij}$ the mean square variation to the distance r_{ij} and $j_0(x)=\sin x/x$ a zeroth order spherical Bessel function. $\sum$ is over all the nuclei in the molecule. With respect to γ_{ij}, we assume that $\gamma_{ij}=1/2D_{ij}^2 r_{ij}$, where D_{ij} is estimated to be 0.06 $\text{Å}^{1/2}$ per Å for all distances in the same molecule.[1,2,6,12]

In the observed $S_m(Q)$ curves marked features are found as follows: the height of the first peak at *ca.* $Q=1.8$ Å^{-1}, a doublet of the hump at *ca.* 4 Å^{-1}, a shape of the second peak at *ca.* 7 Å^{-1}, and the peaks at *ca.* 13 and 19 Å^{-1}. With reference to the higher Q region ($Q \gtrsim 6$ Å^{-1} in the present study), being compared with the case of water,[1,2] the intensity of the second peak ($Q \simeq 7$ Å^{-1}) and the bent of the curve at *ca.* $Q=8$ Å^{-1} are distinctive. Then, for determining the intramolecular structure, reproduction of those features of $Q \gtrsim 6$ Å^{-1} is required in our calculation of $f_1(Q)$.

The structure of methyl alcohol molecule CD_3OD is shown schematically in Fig. 2. With respect to the intramolecular parameters, it is assumed that deute-

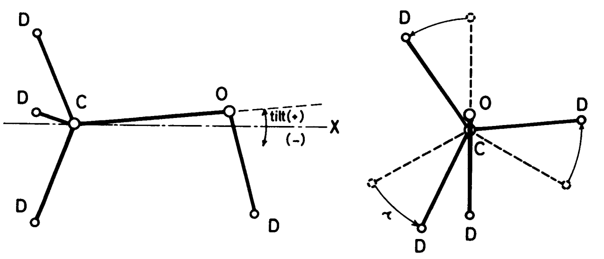

Fig. 2. The structure of deuterated methyl alcohol (CD_3OD) molecule.

Table 2. Range of parameters

Parameter	Range	Interval of variation
$r_{CO}/\text{Å}$	1.420—1.450	0.005
$r_{OD}/\text{Å}$	0.950—1.010	0.005
$r_{CD}/\text{Å}$	1.070—1.100	0.005
DCD/°	105.0—115.0	1.0
COD/°	100.0—125.0	1.0
tilt/°	0.0—3.27	3.27
τ/°	0.0—60.0	2.0

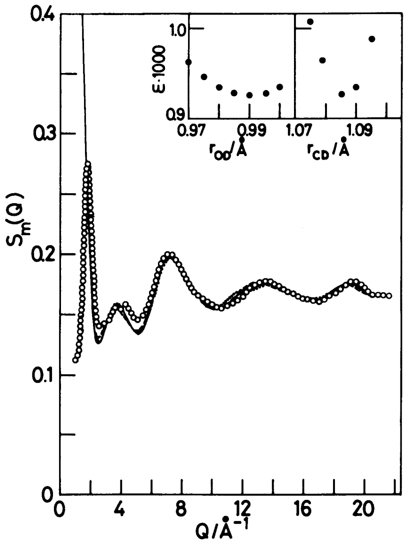

Fig. 3. Observed neutron structure factor $S_m(Q)$ for deuterated methyl alcohol and calculated $f_1(Q)$ curves. ○: Observed $S_m(Q)$, ——: calculated $f_1(Q)$ for the model with fixed methyl group (All parameters used are given in the upper row in Table 3.), ($\varepsilon=0.9282\times10^{-3}$), ----: calculated $f_1(Q)$ curves for the model with freely rotating methyl group (All parameters used are given in the lower row in Table 3.), ($\varepsilon=0.9880\times10^{-3}$), ······: calculated $f_1(Q)$ curves for the Lees and Baker model[3] ($\varepsilon=1.3213\times10^{-3}$). ε is a measure for indicating the deviations of $f_1(Q)$ from the experimental data, and is expressed as

$$\varepsilon = (\sum_i^N\{S_m(Q)_{\text{obsd}}-f_1(Q)_{\text{calcd}}\}^2)^{1/2}/\sum_i^N S_m(Q)_{\text{obsd}},$$

where N is the number of data points in the fitting range of Q, 6—18 Å^{-1}. Variation of ε with distances r_{OD} and r_{CD} is shown in the insets.

rium atoms in the methyl group rotate about the methyl axis (defined as C–X axis in Fig. 2), and that the three C–D bonds in the methyl group are equivalent as well as the three DCD angles. Then, we characterize the molecular structure by seven structural parameters, *i.e.* the bond lengths r_{OD}, r_{CO}, r_{CD}, the DCD angle in the methyl group, the hydroxyl angle COD, the tilt angle and the methyl rotation angle τ (Fig. 2). In order to determine the molecular parameters, $f_1(Q)$ were calculated for more than 12000 models by using Eq. 1 and the curves obtained were compared with the observed $S_m(Q)$ data in the higher Q region ($Q \gtrsim 6$ Å^{-1}). The magnitudes of the parameters were varied in reference to the values given in Table 2.

Results and Discussion

Determination of Intramolecular Parameters for Liquid Methyl Alcohol. By making the calculated $f_1(Q)$ curves fit with the observed $S_m(Q)$ data, we have determined the best structural model for liquid methyl alcohol as follows: $r_{OD}=0.990\pm0.010$ Å, $r_{CO}=1.435\pm0.005$ Å, $r_{CD}=1.085\pm0.005$ Å, DCD=109.5±0.5°, COD=112.0±3.0° and tilt=0.0±3.0°.

Concerning the best structural model, slight arbitrariness still remains in its detailed structure. The methyl rotation angle τ was not decided uniquely in the present study, and the following two models remains undiscriminated as the best ones (Fig. 3): the one is that with $\tau=15.0\pm3.0°$ and the other that with free rotation of methyl group (Table 3). Taking account of the symmetry of the arrangement of deuterium atoms in the methyl group, the two models are regarded as effectively identical with each other. As seen in Table 3, the molecular parameters of the two best models are essentially in good agreement on the whole, though slight discrepancy is observed for the COD angle (and, of course, for the methyl rotation angle τ). The best fit $f_1(Q)$ curves with the experimental data are shown in Fig. 3, including the curve calculated by using Lees and Baker's parameters for gaseous molecules[3] for comparison. Variations of ε with the C–D and O–D bond lengths for the model of fixed methyl group ($\tau=15.0°$) are also shown in Fig. 3.

The best structural parameters determined are tabulated in Table 4, together with those by Montague *et al.*[9] and by Magini *et al.*,[12] where the values also determined in gaseous and crystalline states are shown.

Variation of the Structure of Molecules in Liquid State from that in Gaseous State. The $f_1(Q)$ curve calculated by using the molecular parameters given by Lees and Baker[3] (microwave spectroscopy) is shown in

TABLE 3. MOLECULAR PARAMETERS DETERMINED BY NEUTRON DIFFRACTION METHOD

r_{CO}/Å	r_{OD}/Å	r_{CD}/Å	DCD/°	COD/°	tilt/°	τ/°	$\varepsilon\times10^3$
1.435	0.990	1.085	109.5	109.5	0	15.0	0.9282
1.440	0.985	1.090	109.5	115.0	0	free	0.9880

With respect to ε, see Fig. 3.

TABLE 4. COMPARISON OF INTRAMOLECULAR PARAMETERS OBTAINED FOR METHYL ALCOHOL MOLECULE IN THE PRESENT STUDY WITH THOSE OBTAINED BY OTHER WORKERS

	$\frac{r_{CO}}{Å}$	$\frac{r_{OD}}{Å}$	$\frac{r_{CD}}{Å}$	$\frac{COD}{°}$	$\frac{DCD}{°}$	$\frac{tilt}{°}$	$\frac{\tau}{°}$
Liquid							
Present	1.435±0.005	0.990±0.010	1.085±0.005	112.0±3.0°	109.5±0.5°	0±3.0°	15.0±3.0°, free
Montague *et al.*[a]							
$\lambda=0.5$ Å	1.411±0.009	1.030±0.011	1.070±0.004	99.7±2.2°	(108°38′)	(3°16′)	—
$\lambda=0.7$ Å	1.424±0.004	1.027±0.008	1.062±0.002	103.4±1.2°	(108°38′)	(3°16′)	—
Magini *et al.*[b]	1.437						
Gas							
Lees and Baker[c]	1.4246	0.9451	1.0936	108°32′	108°38′	3°16′	—
	±0.0024	±0.0034	±0.0032	±29′	±42′	±11′	—
Kimura and Kubo[d]	1.428±0.003	0.960±0.05	1.095±0.010	109°±3°	(109°28′)	—	—
Nishikawa[e]	1.427	0.953	1.096	108°24′	109°04′	3°18′	—
Venkateswarlu and Gordy[f]	1.427±0.007	0.956±0.015	1.096±0.01	108°52′±2°	109°02′±45′	3°20′	—
Crystal							
Tauer and Lipscomb[g]	1.42 at −110 °C						
	1.44 at −160 °C						

a) Neutron diffraction at reactor, Ref. 9. b) X-Ray diffraction, Ref. 12. c) Microwave, Ref. 3. d) Electron diffraction, Ref. 6. e) Microwave, Ref. 4. f) Microwave, Ref. 5. g) X-Ray diffraction, K. J. Tauer and W. N. Lipscomb, *Acta Crystallogr.*, **5**, 606 (1952). The values in parentheses were assumed.

Fig. 3, together with the present $S_m(Q)$ data in liquid phase. In the range of $Q \gtrsim 6$ Å^{-1}, a significant disagreement is seen between the present $S_m(Q)$ curve and Lees and Baker's one. This is ascribed to the variation of the intramolecular structure of molecules within liquids in comparison with that in gaseous state, as seen in Table 4.

The most remarkable change of intramolecular parameters from liquid to gaseous state is that in the O–D distance. As seen in Table 4, the O–D distance determined in the present study is 0.990±0.010 Å, and a stretching of the bond length compared with that in gaseous phase, 0.945—0.960 Å,3–6) is obvious. The magnitude of this stretch is found to be similar to the case in water: from 0.96 Å in gaseous state to 0.98 Å in liquid state.1,2) With respect to the nearest intermolecular O···O distance, Magini *et al.*12) reported recently the value of about 2.8 Å from the result by their X-ray diffraction experiment on liquid methyl alcohol. The value is nearly identical with the nearest O···O distance in liquid water.1,2) These all results support an idea that, concerning the distances, r_{OD} and $r_{O\cdots O}$, the situations in hydrogen bonded state are quite similar between the two liquids, methyl alcohol and water.

With respect to other molecular parameters (C–O distance, C–D distance, DCD angle and tilt angle), the following features are pointed out. The present value of C–O distance is 1.435±0.005 Å. This is in good agreement with the value given by Magini *et al.* (1.437 Å) in liquid phase,12) and is longer than that in gaseous systems, 1.425—1.428 Å.3–6) Concerning the methyl group, a slight shortening of the C–D distance and a slight increase of the DCD angles are observed in comparison with those in gaseous state. As described in the preceding item, it is found that the tilt angle becomes zero in liquid state. On the other hand, the angle is observed to be 3°09′—3°30′ in gaseous phase.3–5)

In a recent neutron diffraction study on liquid CD_3OD by means of the reactor conventional method, Montague *et al.*9) have reported a result on the structure analysis of the liquid, and the molecular parameters determined are listed up together in Table 4 for comparison. Noticeable discrepancies between the present results and theirs are found, especially with respect to the O–D distance. The O–D distance assigned by Montague *et al.*, 1.03 Å, is fairly longer than that for heavy water, 0.98 Å, and still longer than that in heavy ice-I (1.01 Å).13) This is clearly unreasonable.

Concluding Remarks

A neutron diffraction study of liquid methyl alcohol (CD_3OD) by means of the LINAC-TOF method was performed, and the geometry of molecules within the liquids was determined. The present study has made it clear that the LINAC-TOF neutron diffraction method is useful in determining the molecular structure in liquid state. And then, due to a series of recent successful results on D_2O,1,2) CD_3COCl,10) and CD_3OD *etc.* by our group, the present LINAC-TOF neutron diffraction method may be said to have been established as a means for the structure analysis of molecular fluids.

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