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X-RAY DIFFRACTION STUDIES OF LIQUID METHYLCYCLOHEXANE $C_6H_{11}-CH_3$ STRUCTURE AT 293 K

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Abstract: The structure of methylcyclohexane $C_6H_{11}-CH_3$ at 293 K was investigated using the X-ray diffraction method. An angular distribution of X-ray radiation scattered in liquid methylcyclohexane was measured. The observable range of scattering angles was $6° \le 2\Theta \le 120°$. Monochromatic radiation MoK_α enabled determination of the scattered intensity between $S_{min} = 0.925$ Å^{-1} and $S_{max} = 15.313$ Å^{-1}. The electron density radial distribution function was calculated. Structural parameters, the mean distances between the neighbouring molecules as well as the coordination numbers were found. The structural data obtainable by X-ray analysis for the liquid studied were discussed.

Streszczenie: Obrazy dyfrakcyjne badanych próbek ciekłego metylocykloheksanu $C_6H_{11}-CH_3$ otrzymano za pomocą dyfraktometru rentgenowskiego TUR−M62 z lampą rentgenowską o anodzie molibdenowej. Promieniowanie charakterystyczne lampy monochromatyzowano płaskim kryształem grafitowym. Badane próbki umieszczono w termostatowanych kuwetach, a pomiary wykonano w temperaturze 20°C ± 0.1°C. Funkcje rozkładu natężenia rozproszonego promieniowania rentgenowskiego zostały wyznaczone w zakresie kątowym od 3° do 60°. Niskokątową część tych funkcji ekstrapolowano do początku układu współrzędnych, co zaznaczono na rysunku linią przerywaną. W celu przeprowadzenia ilościowej analizy struktury metylocykloheksanu, wyznaczono funkcję rozkładu radialnego gęstości elektronowej, na podstawie zmodyfikowanego równania Warrena-Kruttera-Morningstara. Obliczono średnie parametry strukturalne: odległości wewnątrz- i międzymolekularne, liczby koordynacyjne oraz współczynnik upakowania molekuł. Metylocykloheksan nie był dotychczas badany metodami dyfrakcyjnymi w fazie ciekłej.

1. Introduction

X-ray diffraction study of liquids is based on the Fourier analysis of reduced intensity $i(S)$ function. This function is defined [1] as:

$$i(S) = [I_{eu}(S)/N - \sum_{uc} f_j^2(S)]/g^2(S),$$

where $I_{eu}(S)/N$ is the experimentally observed total coherent intensity of scattered radiation per one structural unit, denotes the theoretical independent scattering on atoms of one structural unit, $\sum_{uc} f_j^2(S)$ is a sharpening factor, often written in the form: $\sum_{uc} f_j$ or $\sum_{uc} f_j / \sum_{uc} Z_j$. In order to determine $i(S)$ from the experimental data, $I(S)/N$ and $\sum_{uc} f_j^2$ must be given in the same units.

2. Experimental

The structure of liquid methylcyclohexane $C_6H_{11}-CH_3$ was studied by diffraction of strictly monochromatic X-ray diffraction. For each of these samples, a cuvette with 0.01 mm thick windows of styroflex foil containing a 3 mm thick layer of the studied sample was installed on a X-ray goniometer. The measurements of scattered radiation intensity were performed in a wide range of wave vector ($S_{min} = 0.925$ Å^{-1} to $S_{max} = 15.313$ Å^{-1}), with the use of X-ray radiation MoK_α ($\lambda = 0.71069$ Å). The radiation was monochromatized by reflection from the (002) planes of flat graphite with the angle of monochromatization of $\Theta_m = 6°0'$ ($\Delta\Theta_m = 2.2'$). The X-ray diffraction patterns were recorded on a typical X-ray diffractometer equipped with a special cell for measurements of liquids, described by North and Wagner [2]. In each case, the experimental function of angular distribution of the scattered X-ray intensity was corrected to include the polarization and absorption factors [3], and then normalized [4]. Absorption in the cuvette windows was neglected. Small-angle scattering results ($0° < \Theta < 3°$) were extrapolated to the origin of the coordinate system using second-order functions.

3. Results and discussion

The normalized angular-distribution function I(S) (where $S = 4\pi\sin\Theta/\lambda$) of the studied compound is presented in Fig. 1. The positions of the maxima on this function were found using the Lagrange polynomials method [5]. In the range of 0.92 Å^{-1} < S < 2.60 Å^{-1} the peak positions were determined with accuracy of $\Delta S = \pm 0.01$ Å^{-1}. In the range of 2.60 Å^{-1} < S < 4.50 Å^{-1} the accuracy was $\Delta S = \pm 0.02$ Å^{-1} and in the remaining range was $\Delta S = \pm 0.03$ Å^{-1}.

The most probable intermolecular distances were found from the positions of the maxima of the electron density radial distribution function (EDRDF) (Fig. 2). The first four maxima were ascribed to the interferences within the methylcyclohexane molecule.

The most probable simple configurations of neighbouring molecules in the liquid in question can be examined by fitting the positions of the maxima of the EDRDF to the distances between the centres of neighbours, result-

ing from their van der Waals models. Such models can be constructed on the basis of the bond lengths within the molecule and of the van der Waals radii of C and H atoms. The size of a methylcyclohexane molecule is 7.9 Å (length) × 7.3 Å (width) × 3.5 Å (height).

4. Conclusions

The methods employed allowed a determination of the mean structural parameters (the inter- and intramolecular distances) and local ordering of molecules in liquid methylcyclohexane. The appearance of distinct maxima in the angular distribution function of X-ray scattered radiation and radial distribution function of electron density obtained for liquid methylcyclohexane indicates the presence of a short-range ordering in methylcyclohexane up to a distance of about 20 Å.

The results of this paper permit the following conclusions concerning X-ray analysis of liquid methylcyclohexane structure to be drawn:

- in the liquid methylcyclohexane the molecules are arranged with their cyclohexyl rings in parallel,
- the mean distance calculated for two molecules of methylcyclohexane in the antiparallel arrangement between the carbon atoms of the functional groups $(CH_3)_1 \cdots (CH_3)_2$ is 8.3 Å.

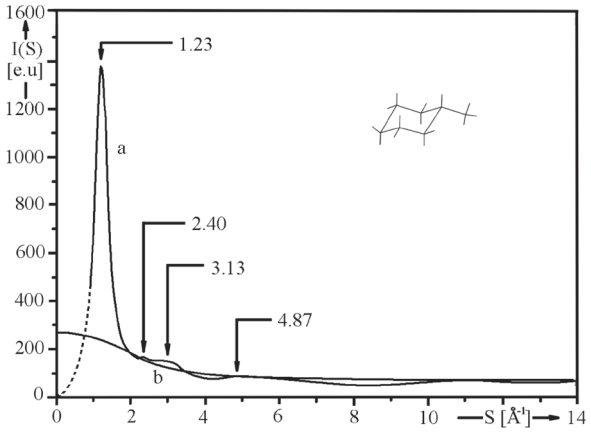

Figure 1. Intensity distributions of X-radiation scattered by methylcyclohexane; a) experimental curve, b) theoretical curve ($I = I_{coh} + I_{incoh}$).

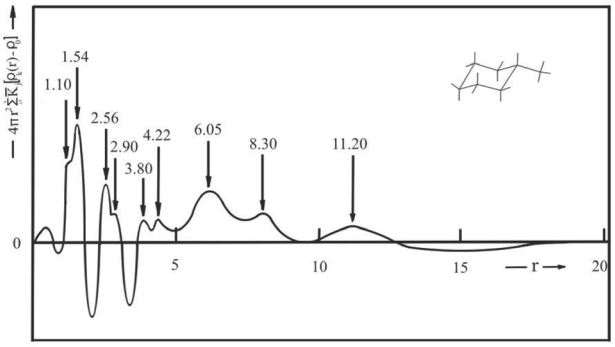

Figure 2. The values of radial distribution function of electron density .

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