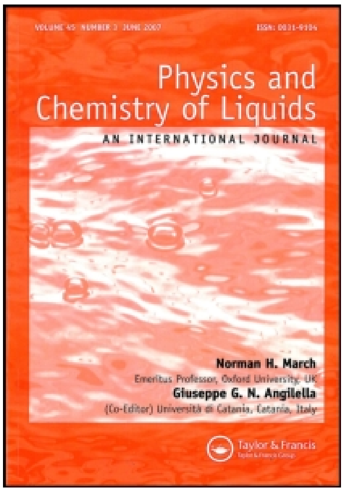

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THE USE OF THE COHEN–TURNBULL MODEL FOR CALCULATION OF THE SELF-DIFFUSION COEFFICIENTS OF LIQUID DICHLOROALKANES

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The paper presents the self-diffusion coefficients calculated for liquid dichloroalkanes $C_6H_{12}Cl_2$, $C_8H_{16}Cl_2$, $C_{10}H_{22}Cl_2$ and $C_{12}H_{24}Cl_2$, with the use of the Cohen and Turnbull model. Determination of self-diffusion coefficients permits a separate analysis of intra- and intermolecular motions and provides information on geometrical and dynamical properties of molecules. The self-diffusion coefficients of selected dichloroalkanes have been determined by X-ray diffraction and compared with the corresponding NMR results. The suitability of the Cohen–Turnbull model of the translating motion for prediction of self-diffusion coefficients for molecules whose shape significantly differs from the spherical symmetry is analysed. Angular distributions of X-ray scattered intensity were measured, and differential radial distribution functions of electron density (DRDFs) were calculated. The mean coordination numbers were obtained from the area delimited by the minima of the DRDFs, and their dependence on the length of the methylene chain is also presented subsequently. On the basis of the DRDFs the average free volume of the molecules and total free volume of the liquids were calculated. The activation volume of the diffusion was found to make about 0.6 of the van der Waals volume of the molecule. As expected the diffusion coefficients decrease with increasing molecular weight. The equation relating the self-diffusion coefficient with the volume of the coordination spheres in the liquid has been derived.

Keywords: Self-diffusion coefficients; Model of Cohen and Turnbull; Differential radial distribution functions; Dichloroalkanes

1. INTRODUCTION

There is no single universal and general theory of the liquid state that would permit a description of translational molecular movement. The calculation of self-diffusion coefficient requires a choice of an appropriate model. For simple liquids whose molecules are spherically symmetrical, translational motion can be sufficiently well described by the hydrodynamical models [1]. For molecules of high anisotropy of shape it is difficult to get a correct theoretical description of this type of motion.

The study was performed for dichloro derivatives of *n*-alkanes (Table I) whose molecules length depends on the number of methylene group repetition. These compounds

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TABLE I Molecular weight M, melting point T_m, boiling point T_b, temperature of measurements T, macroscopic density d and the number of electrons in the molecules of the liquids studied $\sum_j Z_j$

Liquids	*Chemical formula*	M (g/mol)	T_m (K)	T_b (K)	T (K)	d (g/cm^3)	$\sum_j Z_j$
1,6-Dichlorohexane	$Cl(CH_2)_6Cl$	155.07	260	390	293	1.068	82
1,8-Dichlorooctane	$Cl(CH_2)_8Cl$	183.12	265	515	293	1.026	98
1,10-Dichlorodecane	$Cl(CH_2)_{10}Cl$	211.18	288	415	293	0.999	114
1,12-Dichlorododecane	$Cl(CH_2)_{12}Cl$	239.23	302	572	313	0.953	130

are derivatives of saturated hydrocarbons formed by a substitution of two hydrogen atoms with two chlorine atoms at the end of the aliphatic chain.

Dichloroalkanes form a homologue series of the general formula $C_nH_{2n}{-}Cl_2$, where n stands for the number of carbon atoms in the molecule. The shape of the liquid molecules is an extended ellipsoid. Dichlorohexane and dichlorodecane of 99% purity were purchased at Aldrich-Chemie, Germany, dichlorooctane and dichlorododecane – at Janssen-Chimica, Belgium.

2. EXPERIMENTAL

The structure of liquid dichloroalkanes (Table I) was studied by diffraction of strictly monochromatic X-ray radiation. The X-ray diffraction patterns were recorded on a standard X-ray diffractometer equipped with a special cell for measurements of liquids, described by North *et al.* [2] and Drozdowski [3]. The diffracted X-pulses are counted in the time of 40 s, for the diffraction angle ranging from $3° \leq \Theta \leq 60°$, measured with the accuracy $0.005° \leq \Delta\Theta \leq 0.1°$. The angular distribution of the X-ray scattered intensity was measured by applying MoK_α ($\lambda = 0.71069$ Å) radiation. Monochromatization was obtained with a graphite crystal. The measurements were performed using the transmission technique with the incident and diffracted beam symmetric upon the flat sample surface. The method is described in details in [2–5].

In each case, the experimental function of angular distribution of the scattered X-ray intensity was corrected to include the polarization and absorption factors [6], and then normalized [7]. Absorption in the cuvette windows was neglected.

3. CALCULATIONS

The Cohen and Turnbull model [8] assumes that a given central molecule is confined in a cell made by the surrounding molecules. The central molecule can perform restricted movements and its diffusion is blocked. As a result of molecular fluctuations in a liquid, the neighboring molecules can move forming a gap allowing the central molecule to move over a distance of its diameter. Taking into account the probability of the gap creation the diffusion coefficient in this model can be expressed as

$$D = g\,\bar{a}\,\bar{v}\,\exp\left[-\xi\frac{\bar{V}_C}{\bar{V}_F}\right] \tag{1}$$

where g is the geometrical factor usually assumed as equal 1/6, $\bar{a}$ is approximately the molecule diameter, ξ is a constant varying from 0.5 to 1.0. The mean velocity of a molecule, $\bar{v}$, related to its mass is

$$\bar{v} = \left(\frac{3kT}{m}\right)^{1/2}. \tag{2}$$

The volume $\bar{V}_C$ of the critical void must be at least equal to that of the diffusing molecule, the average free volume per molecule $\bar{V}_F$ is a difference between the void volume and the molecule volume $\bar{V}_m$

$$\bar{V}_F = \bar{\alpha}\bar{V}_m(T - T_0). \tag{3}$$

In the above expression $\bar{\alpha}$ is the mean thermal expansion coefficient of the liquid. At T close to the temperature of vitrification T_0, the free volume disappears and the value of the self-diffusion coefficient D, predicted by this theory can be calculated from the formula:

$$D = g\bar{a}\bar{v}\exp\left[-\xi\frac{\bar{V}_C}{\bar{\alpha}\bar{V}_m(T - T_0)}\right]. \tag{4}$$

In order to calculate the self-diffusion coefficients from Eq. (1), it is necessary to know the free volume per molecule. As follows from the Cohen and Turnbull theory [8], the average free volume per molecule is related to the volume $\bar{V}_{\text{elips}}$ through the coefficient of thermal expansion $\bar{\alpha}$ by:

$$\bar{V}_F = \bar{V}_{\text{elips}}\left[\exp\left(\int_{T_0}^{T}\bar{\alpha}\,dT\right) - 1\right], \tag{5}$$

where T_0 is the temperature at which free volume disappears.

The Cohen and Turnbull model has been partly verified by Macedo and Litowitz [9], who have taken into regard the activation energy of molecular jumps.

The Warren–Krutter–Morningstar method [10] was applied to obtain the differential radial distribution functions $4\pi r^2 \sum_{j,k}^{n}[\rho_k(r) - \rho_0]$. The integrals appearing in the expression for $\rho_k(r)$ were found numerically by the Simpson method for $0 \leq r \leq 20$ Å at every 0.05 Å. The radial distribution functions were calculated with the use of the computer program written by Drozdowski [5]. The calculations were performed for the values of the structural parameters of liquid dichloroalkanes collected in Table II. The electron densities of the liquids decrease with increasing chain from 0.342 el/Å^3 ($C_6H_{12}Cl_2$) to 0.314 el/Å^3 ($C_{12}H_{24}Cl_2$).

TABLE II Structural parameters of liquid dichloroalkanes

Parameters	*Liquids*			
	Cl(CH₂)₆Cl	*Cl(CH₂)₈Cl*	*Cl(CH₂)₁₀Cl*	*Cl(CH₂)₁₂Cl*
$\bar{K}_H$ (el)	0.309	0.314	0.318	0.321
$\bar{K}_C$ (el)	5.942	6.124	6.264	6.375
ρ (el/Å^3)	0.342	0.333	0.327	0.314

Where ρ is the mean number of electrons in a unit volume (1 Å^3), and $\bar{K}_H$, $\bar{K}_C$ are the mean effective numbers of electrons in the atoms of hydrogen and carbon.

4. RESULTS

The normalized angular-distribution functions $I(S)$ (where $S = 4\pi \sin\Theta/\lambda$) of all dichloroalkanes studied (Fig. 1) have one main and some smaller diffuse maxima. The positions of the main maximum of the angular intensity distributions $S_1 = (1.42 \pm 0.01)\,\text{Å}^{-1}$ were substituted to the Braggs equation [10] to find the mean distance between the scattering centres in the liquids studied $\bar{d} = (4.43 \pm 0.10)\,\text{Å}$ and the least mean intermolecular distance [11] $\bar{R} = (5.14 \pm 0.15)\,\text{Å}$.

The second maximum occurs at $S_2 = (3.01 \pm 0.02)\,\text{Å}^{-1}$ for all alkanes studied. The third appears at $S_3 = (5.23 \pm 0.03)\,\text{Å}^{-1}$ for dichlorooctane and dichlorodecane, and at $S_3 = (5.29 \pm 0.03)\,\text{Å}^{-1}$ for dichlorohexane and dichlorododecane. The fourth maximum occurs at $S_4 = 8.25\,\text{Å}^{-1}$ for dichlorooctane, at $8.30\,\text{Å}^{-1}$ for dichlorohexane and dichlorodecane and at $8.36\,\text{Å}^{-1}$ for dichlorododecane.

The Fourier analysis of the normalized curves of the scattered radiation intensity gave the differential functions of radial distribution $4\pi r^2 \sum_{j,k}^{n} \bar{K}_j[\rho_k(r) - \rho_0]$. These functions are determined by the structure integral $2r/\pi \int_{S_1}^{S_2} Si(S)\sin(Sr)\,dS$, calculated by the numerical Simpson method for $0 < r \leq 20\,\text{Å}$, at a step of $\Delta r = 0.05\,\text{Å}$. The course of the DRDF function is shown in Fig. 2. The maxima were found by two methods (similarly as those of the angular intensity distributions): directly reading out their positions from the plots and by the Lagrange interpolation polynomial. The results obtained by these two methods were consistent. On the basis of the known courses of these functions it is possible to determine mean inter- and intramolecular distances (knowing the positions of the maxima of the radial distribution functions) and mean coordination numbers (knowing the areas under the curves in a given

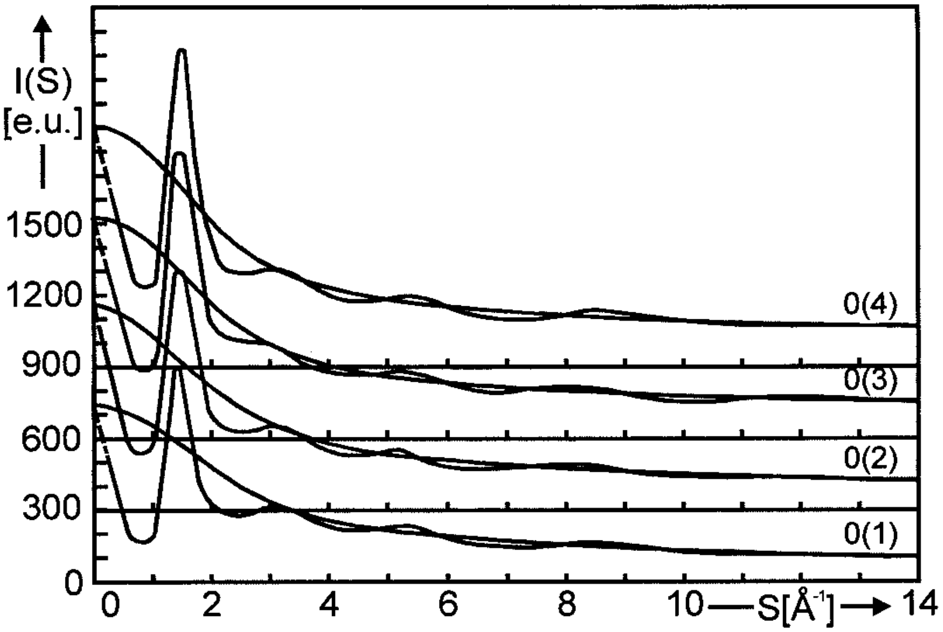

FIGURE 1 Normalized, experimental curves of angular distribution of X-ray scattered intensity in liquid dichloroalkanes ((1) 1,6-dichlorohexane, (2) 1,8 dichlorooctance, (3) 1,10-dichlorodecane, (4) 1,12-dichlorododecane).

range [12]. The DRDFs of all dichloroalkanes studied (Fig. 2) have seven maxima in the range of the distance r below 20 Å. Their positions (Table III) correspond to the most probable interatomic and intermolecular distances in the studied liquids, there are considered in detail below.

The four subsequent maxima in the DRDF function occurring at $\bar{r}_1 = 1.10$ Å, $\bar{r}_2 = 1.55$ Å, $\bar{r}_3 = 1.80$ Å and $\bar{r}_4 = 2.60$ Å, were assigned to the distances between the atoms in the molecules of liquid dichloroalkanes (Fig. 3).

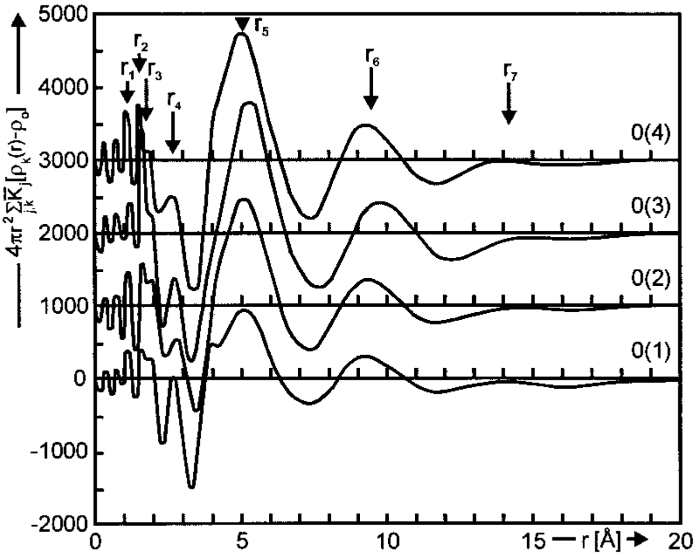

FIGURE 2 Differential radial distribution functions of electron density of liquid dichloroalkanes ((1) 1,6-dichlorohexane, (2) 1,8-dichlorooctane, (3) 1,10-dichlorodecane, (4) 1,12-dichlorododecane).

TABLE III Maxima positions r [Å] of the differential radial distribution functions of electron density of liquid dichloroalkanes

Liquids	*Maxima positions r* (Å)						
	r_1	r_2	r_3	r_4	r_5	r_6	r_7
$C_6H_{12}Cl_2$	1.10	1.55	1.80	2.65	5.00	9.20	14.00
$C_8H_{16}Cl_2$	1.10	1.55	1.80	2.70	5.00	9.30	14.20
$C_{10}H_{20}Cl_2$	1.10	1.55	1.80	2.65	5.05	9.60	14.10
$C_{12}H_{24}Cl_2$	1.15	1.55	1.80	2.60	5.25	9.25	14.50

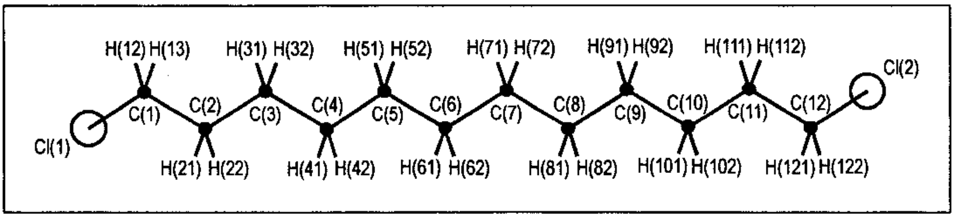

FIGURE 3 Numbering of carbon and hydrogen atoms in the dichloroalkane molecules presented for 1,12-dichlorododecane.

The maxima for $3.5 < r \leq 20\,\text{Å}$ are interpreted as due to intermolecular diffraction and represent the most probable distances between neighbouring molecules. The positions of the minima in the DRDF function are interpreted as corresponding to the ranges of particular coordination spheres [13,14]. The distances $\bar{r}_1, \bar{r}_2, \bar{r}_3$, corresponding to subsequent maxima of these functions for $3.5 < r \leq 20\,\text{Å}$ are the most probable distances between the molecules. The mean radii of the coordination spheres $(\bar{r})$ are manifested as increased electron density [6]. In addition, all the calculated DRDFs showed partial maxima for $0 \leq r \leq 1\,\text{Å}$. These maxima have no physical meaning. Their occurrence seems to be due to the termination-of-series error which is characteristic of all Fourier analyses of diffraction data and results from the inability of diffraction methods to record a truly complete set of experimental intensities [10].

From the known DRDF (Fig. 2) the mean volumes of the spheres [15] and the mean coordination numbers (Table III) were found.

Having determined the mean volumes of the coordination spheres $[\bar{V}_1, \bar{V}_2, \bar{V}_3]$ and the coordination numbers $(\bar{N}_1, \bar{N}_2, \bar{N}_3)$ it was possible to calculate the free volume of molecules $\bar{V}_F$ (the difference between the volume of the void and the molecule volume) and the total free volume of the liquid V_E, defined as the difference between the macroscopic volume of the liquid at a given temperature and the volume occupied by the molecules calculated on the basis of the van der Waals radii (Table V).

The packing coefficient defined by Kitaigorodsky as a ratio of the volume of the molecule to the volume per the molecule in the liquid, for dichloroalkanes takes values from 0.59 to 0.61 (Table VI). These values fall within the range of the packing coefficient values assigned to liquid phase from 0.50 to 0.68 [16]. The packing coefficients calculated by the method proposed by Kitaigorodsky are in agreement with those calculated by DRDFs for particular spheres of intermolecular ordering [17].

The molecular radii (Table VII) were found by comparing the molecule volumes with the volumes of a ball of the same volume and the radius $\bar{a}_k$ [18]. The molecular volumes $\bar{V}_{\text{elips}}$ were found assuming that each molecule can be approximated by

TABLE IV Mean volume of the coordination spheres [Å^3] and the coordination numbers (in parentheses) for liquid dichloroalkanes [15]

Liquids	*Sphere 1*	*Sphere 2*	*Sphere 3*
$C_6H_{12}Cl_2$	1527.5 (6.3)	5089.3 (21.0)	11074.1 (45.7)
$C_8H_{16}Cl_2$	1596.3 (5.4)	4746.4 (16.0)	10939.8 (37.0)
$C_{10}H_{20}Cl_2$	1515.6 (4.3)	4852.4 (13.7)	10465.4 (29.7)
$C_{12}H_{24}Cl_2$	1681.8 (4.0)	5542.1 (13.2)	9795.1 (23.1)

TABLE V Mean values of the total free volume of the liquid V_E [Å^3] and the average free volume of the molecules $\bar{V}_F$ [Å^3] for liquid dichloroalkanes

Liquids	*V_E Spheres*			*$\bar{V}_F$ Spheres*		
	1	2	3	1	2	3
$C_6H_{12}Cl_2$	597.6	1989.7	4328.8	94.9	94.7	94.7
$C_8H_{16}Cl_2$	617.8	1847.2	4235.4	114.4	115.5	114.5
$C_{10}H_{20}Cl_2$	583.8	1893.6	4029.4	135.8	138.2	135.7
$C_{12}H_{24}Cl_2$	688.6	2264.5	4059.4	172.2	171.6	175.7

TABLE VI The van der Waals volume of the molecules $\bar{V}_m$, the volumes per one molecule in the liquid $\bar{V}_C$ and the packing coefficients k

Liquids	$\bar{V}_m$ (Å^3)	$\bar{V}_C$ (Å^3)	k (%)
$C_6H_{12}Cl_2$	147.6	242.3	61
$C_8H_{16}Cl_2$	181.2	295.4	61
$C_{10}H_{20}Cl_2$	216.7	352.0	61
$C_{12}H_{24}Cl_2$	248.3	419.7	59

TABLE VII The lengths of the semiaxes a, b and c and mean molecular radii $\bar{a}_k$ (Å)

Liquids	a	b	c	$\bar{V}_{\text{elips}}$	$\bar{a}_k$	$\bar{a}_{\text{elips}}$
$C_6H_{12}Cl_2$	6.55	2.40	2.25	148.2	3.28	3.28
$C_8H_{16}Cl_2$	7.82	2.40	2.25	176.9	3.51	3.48
$C_{10}H_{20}Cl_2$	9.09	2.40	2.25	205.6	3.73	3.66
$C_{12}H_{24}Cl_2$	10.36	2.40	2.25	234.3	3.90	3.82

an ellipsoid of the semiaxes a, b and c. The molecular volumes calculated by the method of increments (Table VI) are in good agreement with those obtained from the geometrical approximation (Table VII).

5. DISCUSSION

The mean coordination numbers decrease with increasing length of the aliphatic chain (Table III), which can be interpreted as follows. The macroscopic density of liquid dichloroalkanes (Table I) take close values from 1.068 g/cm^3 ($C_6H_{12}Cl_2$) to 0.953 g/cm^3 ($C_{12}H_{24}Cl_2$), whereas their molecular weight (Table I) increases in the homologue series from 155.07 g/mol ($C_6H_{12}Cl_2$) to 239.23 g/mol ($C_{12}H_{24}Cl_2$). Almost in the same volume ($\bar{V}_1 = 1580$Å^3, $\bar{V}_2 = 5060$Å^3, $\bar{V}_3 = 10569$Å^3) there is many more lighter than heavier molecules, which explains the decrease in the mean number of neighbours with increasing length of the chain in the homologue series of the compounds studied. The contribution of the aliphatic chain to the total volume of the spheres increases from approximately 46.3% for $C_6H_{12}Cl_2$ to 55.3% for $C_{12}H_{24}Cl_2$. The contribution of chlorine atoms in the total volume of the sphere decreases from about 14.5% ($C_6H_{12}Cl_2$) to about 8.6% ($C_{12}H_{24}Cl_2$) with increasing length of the chain.

Analysis of Tables III and IV shows that about 39% of the total volume of the liquid is the free volume. The activation volume of diffusion has been estimated as about 0.6 of the molecule volume. A comparison of the molecular volumes with the volumes per a molecule (Table V) indicates that the dichloroderivatives of *n*-alkanes have enough volume in the whole range of fluidity to be able to perform rotation about their long axes. The situation is the same for liquid *n*-alkanes. The critical volume of the void has been estimated as 1.6 of the molecule volume (Table V), which permits the molecule shift over a distance equal to its diameter.

The relaxation times of carbon nuclei measured by ^{13}C-NMR [19,20] suggest a possibility of internal rotations in the long-chain *n*-alkane molecules. In monobromo and dibromo-substituted *n*-alkanes [19] the presence of a heavy atom of bromine

TABLE VIII Self-diffusion coefficients of dichloroalkane molecules D [in $10^{-9}\,\mathrm{m^2/s}$] calculated assuming the Cohen–Turnbull model

Liquids	D (in $10^{-9}\,\mathrm{m^2/s}$)
1,6-Dichlorohexane	0.93
1,8-Dichlorooctane	0.89
1,10-Dichlorodecane	0.87
1,12-Dichlorododecane	0.84

(chlorine) at the end of the hydrocarbon chain leads to significant inhibition of the internal mobility. Results of dielectric relaxation measurements for bromobutane [21] imply that the rate of internal motion is low when compared with that of the reorientational motion of a whole molecule. The attachment of another bromine atom decreases the rate of the internal motion even more [22–24]. Therefore, it is reasonable to assume that the dichloro derivatives of *n*-alkanes occur in the unfolded form and can rotate about the long axes of their molecules (Fig. 3).

The size of the coordination sphere corresponds to the molecular cross-section approximated by an ellipse of the semiaxis $b = 2.40\,\text{Å}$ (Table VI). As follows from Fig. 2 the only geometric arrangement, from among the simplest ones, for which the distances between the mass centres are shorter than 5Å is that with the chains of the neighbouring molecules parallel to one another.

The radius of the first coordination sphere r_1 is the least intermolecular distance and equals $\bar{R} \approx 5.14 \pm 0.15\,\text{Å}$. The mean radius of the second sphere (Fig. 2) corresponds to the distance between the second neighbours in the coordination of the parallel molecules. The coordination in liquid dichloroalkanes should be analysed in the direction perpendicular to the stack of the parallel molecules approximated by ellipsoids (Table VI). The short-range ordering in the dichloroalkanes studied disappears at a distance of ~16.10Å (Fig. 2).

Making use of the notions of the average free volume of the molecule $\bar{V}_F = V_E/\bar{N}$ and the volume of the critical of the void $\bar{V}_C = \bar{V}/\bar{N}$ ($\bar{N}$ is the number of molecules), it can be shown that the fraction $\bar{V}_C/\bar{V}_F$ in Eq. (1) is $\bar{V}_C/\bar{V}_F = \bar{V}/\bar{V}_E$.
Thus, Eq. (1) can be rewritten as

$$D = g\,\bar{a}\,\bar{v}\,\exp\left[-\xi\frac{\bar{V}}{V_E}\right]. \tag{6}$$

As follows from this Eq. (6) to get the self-diffusion coefficient it is necessary to know the volume of the coordination spheres ($\bar{V}$) and the total free volume of the liquid (V_E). The equation relates the rate of diffusion (D) with the molecular parameters ($\bar{V}$, V_E). Table VIII presents the self-diffusion coefficients for the dichloroalkanes studied calculated using Eq. (6). The values calculated in this way are in good agreement with those determined from NMR experiment [25]. Equation (6) predicts a correct order of magnitude of the self-difussion coefficients.

6. CONCLUSIONS

With increasing volume and molecular weight of the dichloroalkane molecules the rate of their translational motion decreases. With increasing length of the methylene chain the mean coordination numbers decrease. The self-diffusion coefficient D, the mean volume of the coordination spheres $\bar{V}$and the total free volume of a given liquid V_E are interrelated by the following equation: $D = g\ \bar{a}\,\bar{v}\ \exp\left[-\xi\bar{V}/V_E\right]$. This equation is based on the concept that statistical redistribution of the free volume occasionally opens up voids large enough for diffusive displacement.

As follows from the above, there is a relation between the radial functions obtained by X-ray diffraction method and the self-diffusion coefficients predicted by the Cohen–Turnbull model. Having determined the volume of the coordination spheres and the free volume of the liquid from the radial distribution function, it is possible to calculate the self-diffusion coefficients of dichloroalkane molecules assuming the Cohen–Turnbull model.

As follows from a comparison of the free volume in the liquid with the volume demanded to allow a rotation of the methylene chain, the molecules of dichloroalkanes can perform rotation about their long axis. The activation volume of diffusion is of about 0.6 of the molecule volume. About 39% of the total volume of the liquid is the free volume. The critical volume of diffusion is close to the molecular volume $\bar{V}_{\mathrm{elips}}$.

The shape and the course of the DRDFs of all studied liquid dichloroalkanes, differing in the length of the methylene chain, are very similar to each other. They are also similar to the DRDFs of liquid *n*-alkanes [26]. The fundamental role determining the arrangement of the dichlorolkane molecules plays a zigzag aliphatic chain. The chlorine atoms determine the molecular orientation. Because of supposed role of the methylene chain in mutual configurations of molecules in liquid dichloroalkanes, it seems very probable that the Cohen–Turnbull model can also hold for other derivatives of *n*-alkanes in the liquid phase.

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