

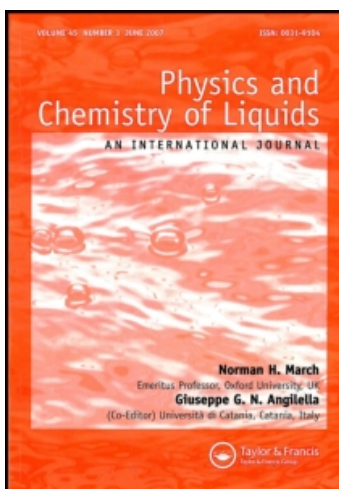
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THE APPLICATION OF THE PERRIN–AGISHEV MODEL FOR CALCULATION OF THE TRANSLATIONAL DIFFUSION COEFFICIENTS OF LIQUID DICHLOROALKANES

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The article presents the translational diffusion coefficients calculated for dichloroalkanes series $C_nH_{2n}Cl_2$ (where $n=6, 8, 10, 12$) in the liquid state, with the use of the Perrin and Agishev model. It has been shown that the molecules of dichloroalkanes assume a mutually parallel arrangement in three possible coordinations. The model of arrangement, orientations and packing of the molecules has been presented. The activation parameters of the compounds studied have been discussed. The physical and structural properties of the liquids studied (macroscopic density, electron density and molecular weight) are correctly described within the van der Waals model predicting their orientations and packing. The formulae linking the diffusion, viscosity and temperature for the liquids have been presented. The assumption that each molecule can be approximated by an ellipsoid of the semiaxes lengths a, b and c has been justified. The translations become slower with increasing volume and weight of the molecule. The diffusion coefficients decrease with increasing molecular weight.

Keywords: Diffusion; X-ray analysis; Model of Perrin and Agishev; Viscosity; Dichloroalkanes

1. INTRODUCTION

The article is a continuation of the author's earlier research work [1,2] on testing the usefulness of the theoretical models of liquids proposed by Cohen–Turnbull and Perrin–Agishev for the calculation of translational diffusion coefficients based on experimental X-ray structural data. It has been shown that for the molecules of the liquids studied the $C(1)–C(2) = 1.54 \text{ \AA}$, $C(1)–C(3) = 2.54 \text{ \AA}$ and $C(1)–C(4) = 3.91 \text{ \AA}$ distances are in agreement with the sp^3 hybridisation of the carbon atoms, and the partial distributions of the maxima in the range $1.10 \text{ \AA} \leq \bar{r} \leq 3.20 \text{ \AA}$ confirm the anti-periplanar conformation of the liquids [2].

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TABLE I Structural and physical parameters of liquid dichloroalkanes

<i>Parameters/liquids</i>	<i>Cl(CH₂)₆Cl</i>	<i>Cl(CH₂)₈Cl</i>	<i>Cl(CH₂)₁₀Cl</i>	<i>Cl(CH₂)₁₂Cl</i>
Mean effective number of electrons per hydrogen atom $\bar{K}_H(\text{el})$	0.309	0.314	0.318	0.321
Mean effective number of electrons per carbon atom $\bar{K}_C(\text{el})$	5.942	6.124	6.264	6.375
Total number of atoms in one molecule $\sum_j \bar{K}_j$	82	98	114	130
Macroscopic density (g/cm ³)	1.068	1.026	0.999	0.953
Molecular mass (g/mol)	155.07	183.12	211.18	239.23
Mean electron density (el/Å ³)	0.342	0.333	0.327	0.314

Dichloroalkanes (Table I) have been studied in the liquid state by the NMR method [3] and by the X-ray diffraction [4]. The method of X-ray scattering and Fourier analysis enabled determination of the mean-structural parameters (inter- and intramolecular distances, radii coordination spheres, coordination numbers and molecule packing coefficients) of the liquids studied.

The compounds to be studied (of 99% purity) were purchased from Aldrich-Chemie (Germany) and Janssen Chimica (Belgium).

2. EXPERIMENTAL

Structural studies were conducted using an X-ray diffractometer equipped with a horizontal counter goniometer HZG3. The source of MoK α radiation was a lamp working at the optimum voltage $U = 55$ kV and current $I = 25$ mA. The X-ray studies of liquid dichloroalkanes have been described in detail in [1,2].

Density of the liquids studied was measured by a pycnometer with a capillary tube, shown in Fig. 1a. The pycnometer was made of Jena glass with tightly fitted lid. The volume of the pycnometer was determined for distilled water as a mean of six measurements. The tightness of the pycnometer was tested by filling with ether and testing the leak. The diameter of the capillary tube was 0.3 mm (see Fig. 1a). The repeatability of weight measurements was to the third decimal digit. The pycnometer was filled with the liquid studied, closed with the capillary tube and placed in the thermostat [5]. After stabilisation of temperature, the pycnometer with the liquid was weighted on an analytical balance to an accuracy of 0.0001 g. The densities were calculated as means of four measurements.

The viscosities of the liquids studied were determined by a capillary Ostwald viscosimeter (Fig. 1b) by measuring the time of flow of a constant liquid volume through the capillary tube. The viscosity was calculated from the formula [6]:

$$\eta = adt, \quad (1)$$

where $a = 0.023$ is a constant characterising the Ostwald viscosimeter, d is the density of the liquid studied and t is the time of the liquid volume flow. Because of a significant effect of temperature on the liquid viscosity the viscosimeter was thermostated (Fig. 1c).

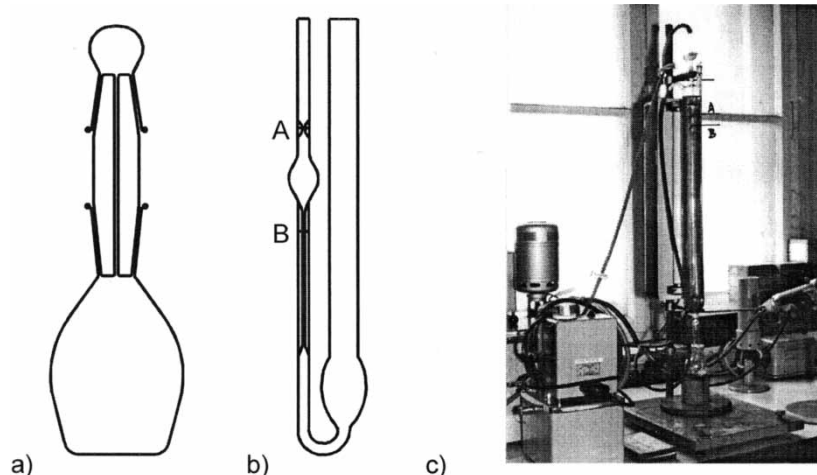


FIGURE 1 (a) The pycnometer with a capillary tube; (b) the capillary Ostwald viscosimeter; (c) the way of thermostating the viscosimeter.

3. CALCULATIONS

The translational diffusion coefficients for molecules in the liquid state can be derived from the simple Stokes–Einstein model as

$$D_t = \frac{kT}{6\pi\eta r}, \quad (2)$$

where k is the Boltzmann constant, T is the temperature in Kelvins, η is the viscosity and r is the molecule radius. Usually this model yields correct D_t values for small spherical or nearly spherical molecules [7].

The Perrin–Agishev model [8,9] describes reorientation of an ellipsoidal molecule under limiting stick conditions. For an axially symmetrical ellipsoid with semiaxes a and $b = c$ one finds:

$$\xi_{xx} = \frac{32\pi b^2 |a^2 - b^2|}{3|2a - b^2 S|} \eta \quad (3)$$

$$\xi_{yy} = \xi_{zz} = \frac{32\pi |a^4 - b^4|}{3|2a^2 - b^2| S - 2a} \eta \quad (4)$$

where a and b are the semiaxes of the ellipsoid and η is the viscosity; $S = 2|b^2 - a^2|^{-1/2} \times \arctg[|b^2 - a^2|^{1/2} a^{-1}]$ for oblate $a < b = c$, and $S = 2|a^2 - b^2|^{-1/2} \ln[|a + \sqrt{a^2 - b^2}| b^{-1}]$ for prolate $a > b = c$ ellipsoid.

The model yields faster reorientation of the molecule around the longer axis irrespective of whether it is the major or minor symmetry axis.

4. RESULTS

The temperature changes in the density of the liquid studied are illustrated in Table II. The maximum uncertainty of density determination was 1%.

Table III gives viscosity coefficients of the *n*-alkane dichloroderivatives studied and determined to the accuracy of 2%.

Based on the differential radial distribution functions (DRDFs) of electron density, the average free volume of the molecules and total free volume of the liquids were calculated [1]. The activation volume of the diffusion was found to make about 0.6 of the van der Waals volume of the molecule.

The values of molecular radii (Table IV) were obtained from a comparison of the specific volumes of the molecules with that of an equivalent ball of the radius \bar{a}_k [10]. The specific volumes of the molecules \bar{V}_{elips} were determined assuming that each molecule can be approximated by an ellipsoid of the semiaxes *a*, *b* and *c*. The volumes calculated by the method of increments [11] are in agreement with those of the geometric approximation (Table IV).

The molecules of dichloroalkanes are mutually oriented in three coordinations: side by side or parallel (Fig. 2), parallel but shifted by about 2.5 Å along the chain axis (Fig. 3) and shifted by 2.5 Å along the chain axis and rotated by 90° (Fig. 4).

TABLE II Temperature dependence *T* (K) of density $d \cdot 10^{-3}$ ($\text{kg} \cdot \text{m}^{-3}$) of 1,6-dichlorohexane, 1,8-dichlorooctane, 1,10-dichlorodecane and 1,12-dichlorododecane

<i>T</i> (K)	$d \cdot 10^{-3}$ ($\text{kg} \cdot \text{m}^{-3}$)			
	<i>Cl</i> (CH ₂) ₆ <i>Cl</i>	<i>Cl</i> (CH ₂) ₈ <i>Cl</i>	<i>Cl</i> (CH ₂) ₁₀ <i>Cl</i>	<i>Cl</i> (CH ₂) ₁₂ <i>Cl</i>
293	1.068	1.026	0.999	0.953
313	1.047	1.007	0.969	0.931
333	1.025	0.994	0.949	0.912
353	1.012	0.975	0.921	0.908

TABLE III Viscosity of 1,6-dichlorohexane, 1,8-dichlorooctane, 1,10-dichlorodecane at 293 K and 1,12-dichlorododecane at 313 K

<i>Liquids</i>	<i>Values of the viscosity coefficient</i> 10^{-4} ($\text{N} \cdot \text{s} \cdot \text{m}^{-2}$)
<i>Cl</i> (CH ₂) ₆ <i>Cl</i>	2.9
<i>Cl</i> (CH ₂) ₈ <i>Cl</i>	4.8
<i>Cl</i> (CH ₂) ₁₀ <i>Cl</i>	7.7
<i>Cl</i> (CH ₂) ₁₂ <i>Cl</i>	10.1

TABLE IV Semiaxes, *a*, *b* and *c*, molecular radii \bar{a}_k (Å³) and van der Waals volume of the molecules \bar{V}_m (Å³)

<i>Liquids</i>	<i>a</i>	<i>b</i>	<i>c</i>	\bar{V}_{elips}	\bar{V}_m	\bar{a}_k	\bar{a}_{elips}
C ₆ H ₁₂ Cl ₂	6.55	2.40	2.25	148.2	147.6	3.28	3.28
C ₈ H ₁₆ Cl ₂	7.82	2.40	2.25	176.9	181.2	3.51	3.48
C ₁₀ H ₂₀ Cl ₂	9.09	2.40	2.25	205.6	216.7	3.73	3.66
C ₁₂ H ₂₄ Cl ₂	10.36	2.40	2.25	234.3	248.3	3.90	3.82

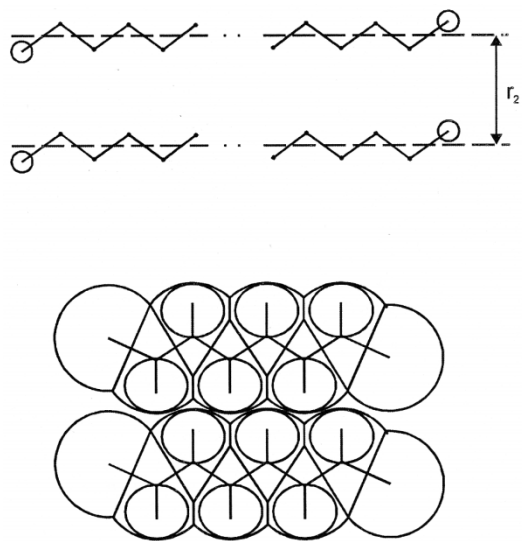


FIGURE 2 Parallel antiperiplanar arrangement of dichloroalkanes molecules.

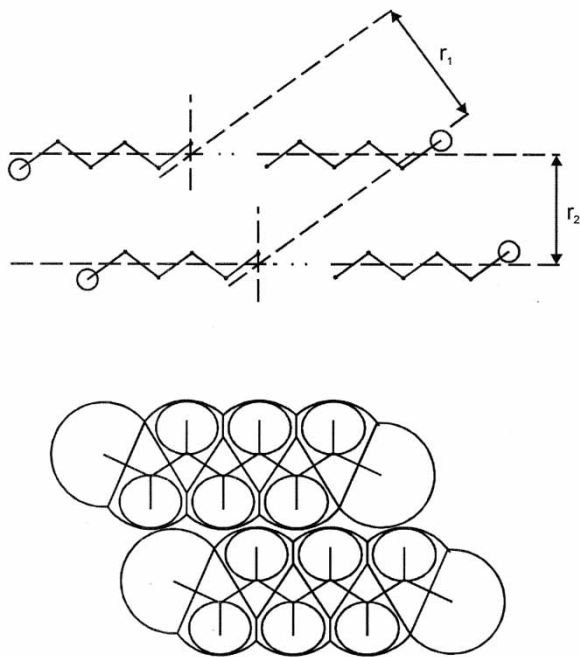


FIGURE 3 Parallel arrangement of dichloroalkanes molecules with a shift by 2.5 Å along the chain.

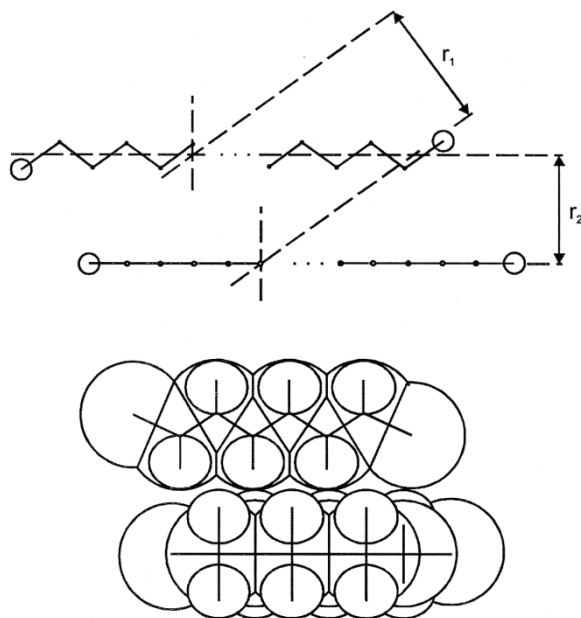


FIGURE 4 The molecular chains are shifted by about 2.5 \AA and rotated at 90° [2].

TABLE V Arrangement of dichloroalkanes molecules and distances between them

<i>Parallel arrangement of molecules</i>	<i>Distance between the mass centres</i>	<i>Distance between the chain axis</i>
Side by side	3.90	3.90
Side by side and shifted	4.90	4.20
Shifted and rotated by 90°	4.65	4.20

TABLE VI Parallel $\xi_{xx} \cdot 10^{-9}$ ($\text{m}^2 \cdot \text{s}^{-1}$) and perpendicular $\xi_{yy} \cdot 10^{-9}$ ($\text{m}^2 \cdot \text{s}^{-1}$) values of the component of self-diffusion coefficients calculated according to the Perrin-Agishev model

<i>Liquids</i>	ξ_{xx}	ξ_{yy}
1,6-Dichlorohexane	0.91	0.47
1,8-Dichlorooctane	0.84	0.42
1,10-Dichlorodecane	0.81	0.40
1,12-Dichlorododecane	0.76	0.38

The shift with the rotation leads to the distance between the mass centers of $r_1 = 4.65 \text{ \AA}$ and the distance between the chain axes $r_2 = 4.20 \text{ \AA}$ (Table V).

Table VI presents the calculated values of the self-diffusion coefficients of dichloroalkanes molecules in the direction parallel to the long axis of the molecule ξ_{xx} and perpendicular to ξ_{yy} .

5. DISCUSSION

The macroscopic densities of dichloroalkanes (Table I) take values from 1.068 g/cm³ (C₆H₁₂Cl₂) to 0.953 g/cm³ (C₁₂H₂₄Cl₂). The molecular mass of dichloroalkanes increases with the homologous series from 155.07 g/mol (C₆H₁₂Cl₂) to 239.23 g/mol (C₁₂H₂₄Cl₂).

As follows from Table III, an increase in the length of the hydrocarbon chain by two methylene groups –CH₂ is accompanied by an increase in the viscosity coefficient.

A relation between the coefficients and the geometric size of the liquid molecule has been presented (Table IV).

Diffusion of the molecules of dichloroalkanes studied can be described as relative shifts of hydrocarbon chains taking place only when they are in specific arrangements (Table V). The orientational (Keesom) forces and the inductive (Debye) forces acting between the molecules of dichloroalkanes prompt the local intermolecular arrangement. The dominant effect on the local structure of the liquid dichloroalkanes is exerted by the shape and length of the methylene chain. The chlorine atoms determine the molecular orientations. Chlorine atoms responsible for negative induction effect ($I = 3.0$) enhance the attraction of the chain molecules. The proposed parallel coordination of molecules is similar in all studied liquids and depends on mutual orientations of the methylene chains of the neighbouring molecules. The molecules tend to assume positions in which their potential energy is minimum [12]. The parallel arrangement of the molecules results in a strong birefringence (difference in the refraction indices of two waves propagating in the same direction) and clear anisotropy of the thermal expansion [5]. 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.

Analysis of the data from Table VI implies that with increasing length of the molecule its translational motion is better described by the self-diffusion coefficient ξ_{xx} . Therefore, the translational motion in the direction of the long axis of the molecule is more probable than in the perpendicular direction [1].

6. CONCLUSIONS

The most important conclusions based on the experimental data and analyses of the Perrin–Agishev model hitherto proposed are as follows.

The molecules of the dichloroalkanes studied can occur in the antiperiplanar conformation (sp³ hybridisation of carbon atoms).

There are three variants of the parallel coordination: with chains side by side, with one chain shifted by about 2.5 Å along the chain axis with respect to the other one and with the chains at the right angle to one another.

About 40% of the total volume of a liquid takes the free volume, while 6–10% of the total volume takes the free volume per molecule, the volume of the critical void is equal to about 1.6 of the volume of the diffusing molecule.

The translations become slower with increasing volume and weight of the molecule.

With increasing length of the aliphatic chain the movement along the long symmetry axis of the molecule becomes more favoured.

Irrespective of the length of the chain, the diffusion of the longer axis of the molecule takes place with a shift by about 2.5 Å.

The results of the study of molecular correlations in liquid dichloroalkanes may be important for explanation of mechanisms of certain physical and chemical processes taking place in similar systems, for example diffusion or thermal conductivity.

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