SHORT−RANGE ORDERING IN *ORTHO*−CHLOROANISOLE AT 293 K BY X-RAY DIFFRACTION

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Structural analysis of liquid *o*-chloroanisole C_7H_7ClO by X-ray monochromatic radiation scattering method was elaborated. The X-ray measurements were made at 273 K for the scattering angle range Θ varying from 3° to 60°. The compounds to be studied of 99% purity were purchased from Koch−Light Laboratories (England).

The short-range arrangement is characterized by the values of the distances between the nearest molecules determined by the so-called radii of coordination spheres and a number of molecules in subsequent coordination spheres around one molecule chosen as central [1].

From the known interatomic distances and valence angles, and assuming the van der Waals atomic radii determined by X-ray methods for crystalline organic compounds, one can construct the *o*-chloroanisole molecule (Fig. 1) and hence perform an analysis of the mutual dispositions of molecules in the liquid.

From the shape of the intensity scattered in liquid *o*-chloroanisole (Fig. 2), most probable intermolecular distances in liquid *o*-chloroanisole can be assigned to the maxima of the distribution function.

The angular distribution of the intensity of scattered X-ray (Fig. 2) is characterized by two general maxima which are responsible for intermolecular interaction. The calculated mean, most often occurring, smallest mutual distances between molecules of liquid *o*-chloroanisole are: $r_1 = 6.66$ Å, $r_2 = 7.15$ Å, $r_3 = 8.23$ Å. Local, most probable manners of packing and mutual orientation of molecules within the space of the first coordination sphere are discussed.

X-ray structural analysis was applied to determine the packing coefficient [2] of *o*-chloroanisole molecules.

Because of the permanent dipole moment of the molecule, *o*-chloroanisole $\mu = 2.85$ D, the neighbouring molecules are arranged so that their dipolar moments are antiparallel. In liquid *o*-chloroanisole only in the antiparallel conformation the distance between the centres of the chlorine groups is Cl−Cl' = 7.15 ± 0.15 Å.

These results can be interpreted in terms of a simple model of local arrangement of molecules, which probably can be valid for a larger class of molecular liquids, i.e. polar monosubstituted derivatives of anisole.

Computer techniques [3] were used to minimise the effects of experimental errors, uncertainties in the scattering factors, and termination errors.
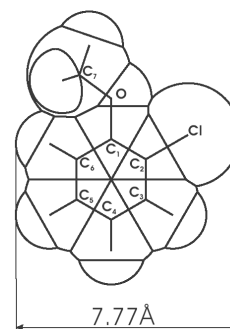

Figure 1. A model of the *o*-chloroanisole molecule structure ($d = 1.123$ g/cm³), with van der Waals radii taken into account.

The packing coefficient of molecules in liquid *o*-chloroanisole is $k = 60\%$.
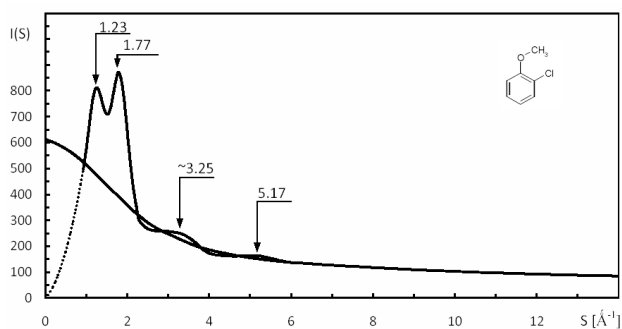

Figure 2. Normalized, experimental curve of angular distribution of X-ray scattered intensity in liquid *o*-chloroanisole.

References

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