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THE STUDY OF ORIENTATIONAL ORDER IN MIXED PLASTIC CRYSTAL $(CH_3)_2CCl_2$ – CCl_4 BY ^1H NMR SPECTROSCOPY

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Abstract ^1H NMR spectra of noncubic plastic single crystals of 2,2-dichloropropane – carbon tetrachloride mixtures have been studied. Orientational order parameters of 2,2-dichloropropane molecules in this phase were determined by computer simulation of NMR spectra.

INTRODUCTION

Plastic crystals are molecular crystals with low entropy of fusion. They are characterized by high rotational mobility of molecules which changes little on melting, and relatively high translational diffusion.[1,2] For improvement in our understanding of the plastically-crystalline state it is important to know the degree of orientational disorder in these crystals. The information on orientational order in one-component cubic plastic crystals may be obtained from optical measurements.[3,4] The degree of orientational order in some noncubic plastic crystals was determined from the value of birefringence,[5] from quadrupolar splitting in ^2H NMR spectra,[6,7] from dipolar splittings in ^1H NMR spectra.[8]

In addition to investigation of one-component plastic crystals it is interesting to study two-component

systems where one from the two components or both have plastic crystal phases. Some experimental investigations of dielectric and thermodynamic properties, X-ray studies and NMR studies of molecular motion in two-component systems were performed.[2]

Here we report the results of ^{1}H NMR investigation of orientational order of 2,2-dichloropropane molecules in the two-component system 2,2-dichloropropane - carbon tetrachloride.

Phase diagram for this system does not seem to be studied.Both component have plastic crystal modifications: 2,2-dichloropropane[2] in the temperature range 239.4 K - 188 K and carbon tetrachloride[9] in 250.4 K - 225.1 K form stable rhombohedral plastic phases.Besides, carbon tetrachloride in solidifying can transform into metastable cubic phase.[9]

EXPERIMENTAL

Sample preparation was the following. 2,2-dichloropropane was fractionally distilled. The melting point, 239.3 K, agreed with the literature value. Chromatographically pure carbon tetrachloride was used with no further purification.The mixtures prepared were sealed into NMR tubes.

For the registration of ^{1}H NMR spectra we used a high resolution spectrometer "Tesla" BS 487C. The probehead was modified to observe the sample through crossed polaroids.With the help of such observation we controlled the quality of single crystals and determined the orientation of crystal optical axis.

On cooling of liquid solutions metastable cubic phase was formed as a rule. When several rhombohedral single crystals were formed the grain boundaries could be

clearly seen. In case of a single crystal the fringe pattern was uniform along the sample. We investigated only those noncubic single crystals which had no defects seen in the polarized light.

RESULTS AND DISCUSSION

Angular dependences of rhombohedral single crystal spectra of different composition were measured.Typical spectra are shown in Figure 1. The analogous dependence was earlier observed in another uniaxial plastic crystal - sulfolane.[8]

In such systems as liquids in external fields, liquid and plastic crystals having one symmetry axis not lower than the third order, in case of rapid enough molecular motion (reorientation, diffusion), for intramolecular dipolar interproton couplings constants the following equation is valid:[8,10]

$$b_{ij}=\frac{\gamma^2 \cdot h}{2\pi r_{ij}^3} \sum_{\alpha,\beta} S_{\alpha\beta}(3\cos\theta_{ij\alpha}\cos\theta_{ij\beta} - \delta_{\alpha\beta})\frac{1}{2}(3\cos\theta_{zH}-1), \quad (1)$$

where γ is gyromagnetic ratio of the proton, r_{ij} is the distance between i and j protons, $\theta_{ij\alpha}$ is the angle between r_{ij} and the molecular axis α, θ_{zH} is the angle between crystal optical axis z and magnetic field, $S_{\alpha\beta}$ is the ordering matrix, $\alpha,\beta = a,b,c$ are the axes of Cartesian system connected with the molecule. Values b_{ij} should be averaged over the methyl groups rotations.

The angular dependence of NMR spectra, Figure 1, is in accordance with the formula (1),i.e. NMR lineshape are defined first of all by intramolecular dipolar intaractions. The order parameters S_{aa} and $S_{bb}-S_{cc}$ of 2,2-dichloropropane molecules obtained by computer simulation of NMR spectra are presented in Figure 2. The a axis lies along

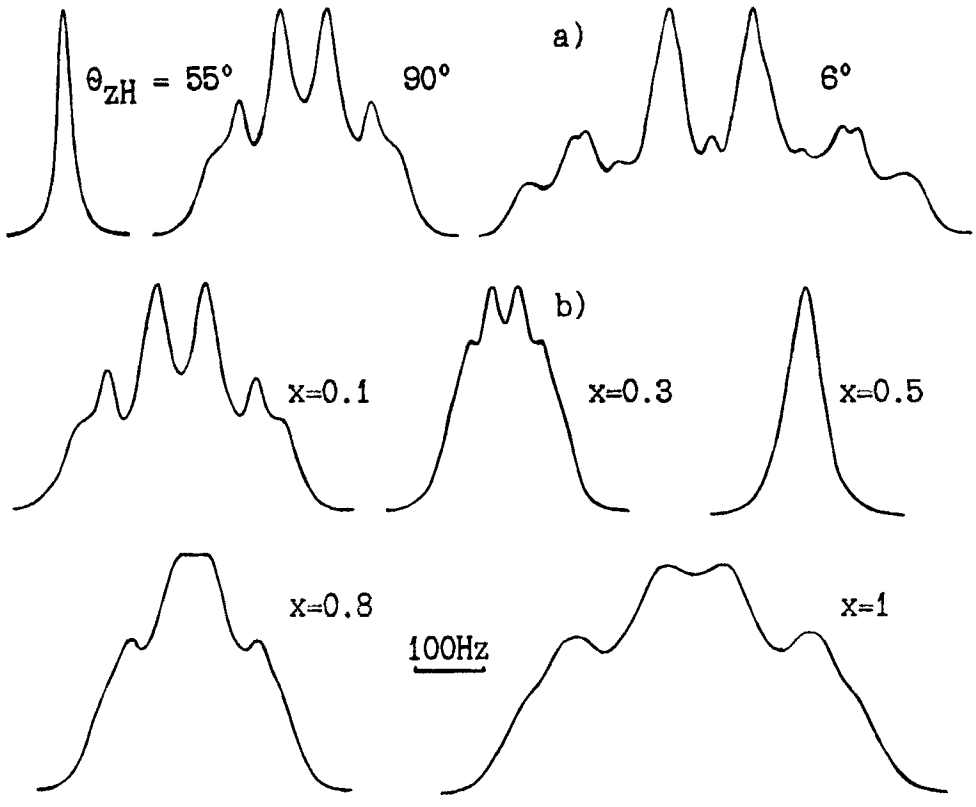

FIGURE 1. PMR spectra of mixed plastic single crystals $(CH_3)_2CCl_2 - CCl_4$. x - mole fraction of $(CH_3)_2CCl_2$.
a) angular dependence, x = 0.1, T = 238 K.
b) concentration dependence, θ_{ZH} = 90°, T = 228 K.

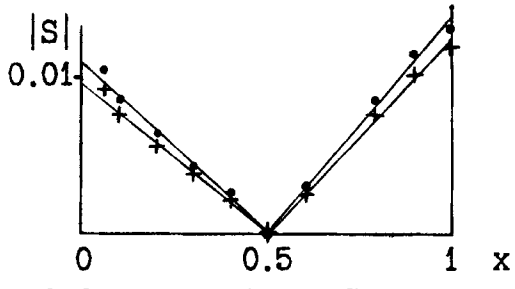

FIGURE 2. Order parameters S_{aa} -• and $S_{bb}-S_{cc}$ -+ of $(CH_3)_2CCl_2$ molecules.

the C_2 symmetry axis, **b** and **c** lie in the two mirror planes, **b** axis connectes **C** atoms of methyl groups.

Both carbon tetrachloride and 2,2-dichloropropane form stable rhombohedral plastic phases with almost identical dimensions of the unit cells.[11] The elements of ordering matrix of $(CH_3)_2CCl_2$ molecules at mole fraction of this substance tending to 0 and 1 are also very close, Figure 2. It is interesting that in the middle range of concentrations the order parameters are tending to zero.

The investigation of the ordering degree in plastic crystals is to great extent analogous to NMR investigations of molecules dissolved in liquid crystal solvents.[10] This is due to the fact that in both cases the values of correlation times for molecular motion are close to those observed in liquids. Note, that the degrees of orientational order in both systems are also very close in spite of different phase conditions of these systems.

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