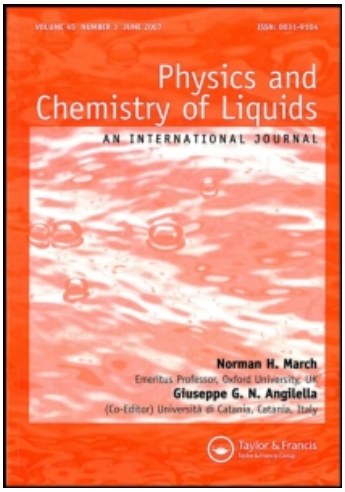

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X-RAY ANALYSIS OF INTERMOLECULAR INTERACTIONS IN SOLUTIONS OF 2-METHYL-2-PROPANOL IN CARBON TETRACHLORIDE

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It was found that the changes in the values of the mean least intermolecular distances with increasing concentration of the solution of 2-methyl-2-propanol in carbon tetrachloride were not linear. Within the range of low concentrations, *i.e.* from 0.07–0.08 molar fraction, a local minimum of the values of the mean least intermolecular distance was found to occur. This value remains stable within the range from 0.1 to 0.6 molar fraction, and then decreases to the minimum value for pure 2-methyl-2-propanol. The results obtained in this work confirm the specific structural properties of the solution in the lower concentration range.

Keywords: X-ray diffraction; intermolecular interactions

1. INTRODUCTION

The solutions of 2-methyl-2-propanole in carbon tetrachloride have already been the subject of earlier resonance studies, in which the hydroxyl NMR frequencies have been measured as function of concentration and temperature [1,2]. The present work has been stimulated by reports on specific physical properties of solutions at low concentrations [3,4]. By using the X-ray diffraction method, the character of changes of the values of the mean least intermolecular distances the solution of 2-methyl-2-propanol in carbon tetrachloride

within a wide concentration range, was studied. The mean values of R were approximately determined from the position of the main maximum in X-ray scattering pattern, which, as known, is the most directly related with the packing of atoms and molecules when compared with other methods. We used the formula [5]:

$$\bar{R} = 7.73/S_{\max} - 0.3, \tag{1}$$

where $S_{\max} = 4\pi\sin\Theta/\lambda, 2\Theta$ the angle of scattering and λ the X-ray scattering wavelength. The correcting factor '0.3' for molecular liquids has been found empirically (Voigtlaender-Tetzner 1958).

2. EXPERIMENTAL

Intensity of radiation scattered by a layer of the studied solution was determined by the transmission method using a typical X-ray

TABLE I Values of the molar concentration, molar mass for pure carbon tetrachloride, solutions of 2-methyl-2-propanol and pure alcohol

Molar concentration X	*Chemical formula*	*Molar mass M[10^3kg/mol]*
0.000	CCl_4	153.8400
0.005	'$C_{1.015}Cl_{3.980}H_{0.05}O_{0.005}$'	153.4414
0.010	'$C_{1.030}Cl_{3.960}H_{0.10}O_{0.010}$'	153.0428
0.020	'$C_{1.060}Cl_{3.920}H_{0.20}O_{0.020}$'	152.2457
0.030	'$C_{1.090}Cl_{3.880}H_{0.30}O_{0.030}$'	151.4485
0.040	'$C_{1.120}Cl_{3.840}H_{0.40}O_{0.040}$'	150.2886
0.050	'$C_{1.150}Cl_{3.800}H_{0.50}O_{0.050}$'	149.8543
0.060	'$C_{1.180}Cl_{3.760}H_{0.60}O_{0.060}$'	149.0571
0.070	'$C_{1.210}Cl_{3.720}H_{0.70}O_{0.070}$'	148.2600
0.080	'$C_{1.240}Cl_{3.680}H_{0.80}O_{0.080}$'	147.4628
0.090	'$C_{1.270}Cl_{3.640}H_{0.90}O_{0.090}$'	146.6657
0.100	'$C_{1.300}Cl_{3.600}H_{1.00}O_{0.100}$'	145.8686
0.200	'$C_{1.600}Cl_{3.200}H_{2.00}O_{0.200}$'	137.8972
0.300	'$C_{1.900}Cl_{2.800}H_{3.00}O_{0.300}$'	129.9258
0.400	'$C_{2.200}Cl_{2.400}H_{4.00}O_{0.400}$'	121.9544
0.500	'$C_{2.500}Cl_{2.000}H_{5.00}O_{0.500}$'	113.9830
0.600	'$C_{2.800}Cl_{1.600}H_{6.00}O_{0.600}$'	106.0116
0.700	'$C_{3.100}Cl_{1.200}H_{7.00}O_{0.700}$'	98.0402
0.800	'$C_{3.400}Cl_{0.800}H_{8.00}O_{0.800}$'	90.0688
0.900	'$C_{3.700}Cl_{0.400}H_{9.00}O_{0.900}$'	82.0974
1.000	$(CH_3)_3COH$	74.1260

diffractometer adapted for measurements of liquids [6,7]. The number of pulses in a chosen period of time was calculated and thus obtained pulse density was recorded. The monochromatic MoKα radiation, $\lambda = 0.71069$ Å, was used. The samples of 2-methyl-2-propanol and of carbon tetrachloride used as a solvent were twice distilled.

The value of molar concentration and molar mass for pure carbon tetrachloride, solutions of 2-methyl-2-propanol and pure alcohol are given in Table I.

The structural formulae in inverted commas, Table I, describe the so-called effective molecules in the solution calculated according to the equation [8]:
"effective molecule" $= \Sigma x_i$ molecule$_i$, where x_i is the molar fraction of the i-th molecule.

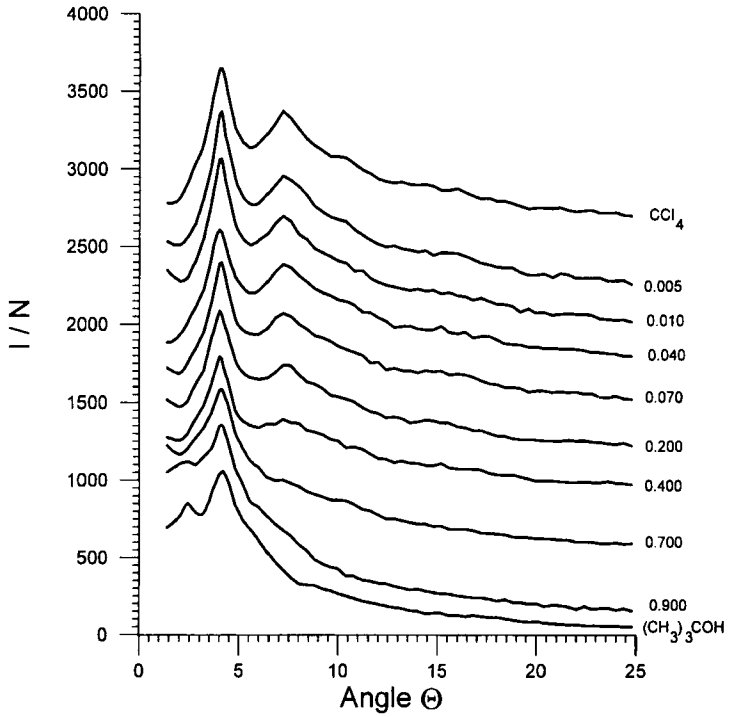

FIGURE 1 Mean angular distributions of the scattered radiation intensity for pure 2-methyl-2-propanol, for alcohol solution in carbon tetrachloride and for pure carbon tetrachloride.

3. RESULTS

From the angular distribution of the scattered radiation intensity, Figure 1, we obtained the mean least intermolecular distance for pure alcohol, for alcohol solution in carbon tetrachloride of molar concentration (X): 0.9; 0.8; 0.7; 0.6; 0.5; 0.4; 0.3; 0.2; 0.1; 0.09; 0.08; 0.07; 0.06; 0.05; 0.04; 0.03; 0.02; 0.01; 0.005 and for pure carbon tetrachloride, Table II.

With increasing concentration the intermolecular distance R at first increases from 5.85 Å to 5.95 Å with respect to that in pure carbon tetrachloride (Table II, Fig. 2) at $X=0.04$ molar fraction. At $X=0.08$, the intermolecular distance reaches a minimum of 5.84 Å.

With concentrations increasing from $X=0.1$ to $X=0.6$, R remains constant and equal to about 5.92 Å, within the error of $\Delta\bar{R} = \pm 0.04$ Å. For higher concentrations R gradually decreases reaching $R=5.69$Å for pure 2-methyl-2-propanol.

TABLE II The position of the main maxima in the experimental curve and the mean value of the least intermolecular distances

Molar concentration X	*Position of the maxima* Θ_{max}	*Mean least intermolecular distances* $\bar{R} \pm 0.04$ [Å]
0.000	4.070	5.85
0.005	4.070	5.86
0.010	4.060	5.87
0.020	4.055	5.88
0.030	4.020	5.93
0.040	4.011	5.95
0.050	4.035	5.91
0.060	4.060	5.87
0.070	4.075	5.85
0.080	4.080	5.84
0.090	4.050	5.89
0.100	4.035	5.91
0.200	4.028	5.92
0.300	4.030	5.92
0.400	4.026	5.92
0.500	4.030	5.92
0.600	4.025	5.92
0.700	4.082	5.84
0.800	4.125	5.78
0.900	4.130	5.77
1.000	4.182	5.69

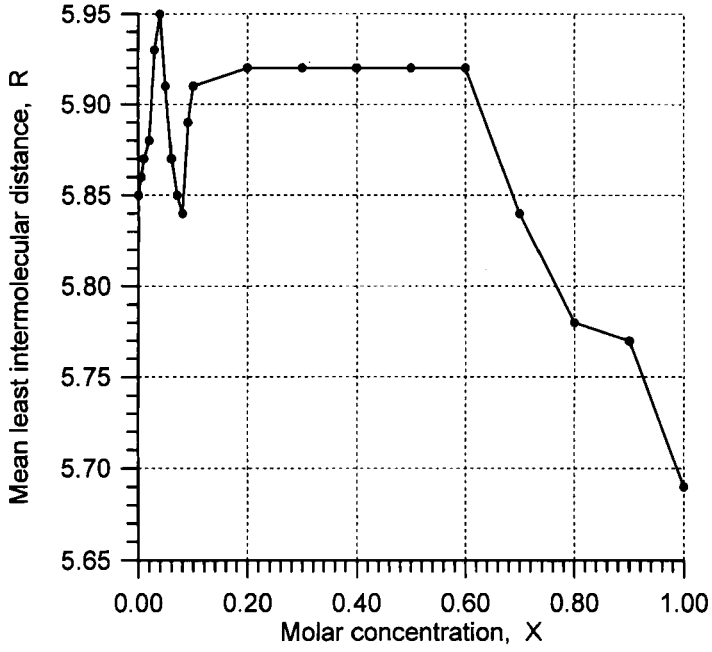

FIGURE 2 The values of the mean least intermolecular distances for various molar concentration of 2-methyl-2-propanol in carbon tetrachloride.

4. CONCLUSIONS

As follows from results of the earlier studies CCl_4 molecules show directional ordering due to the interaction between electron clouds of Cl atoms from the neighbouring molecules [9]. This interaction is manifested as a side maximum for the angle of $\Theta = 7.25°$ in the experimental curves of intensity distribution, Figure 1. With increasing concentration this maximum gradually disappears and is not visible at a concentration $X = 0.8$. Therefore, the occurrence of the minimum R at $X = 0.08$ can be interpreted as a result of penetration of the alcohol molecules into the structure of CCl_4 without any destruction of the characteristic ordering of CCl_4 molecules. It is reasonable to suppose that at low concentrations, the alcohol molecules occur mostly in the monomeric form. In this form the alcohol molecules can easily come among the associates of CCl_4 as their size is smaller than that of CCl_4

molecules. It is known that the molecules of both compounds studied are approximately spherical in shape and their diameters are $2r = 5.69$Å and $2r = 5.85$Å respectively. In the range of higher concentrations, starting from $X = 0.6$, the alcohol molecules form associates which is evidenced by a significant decrease of the intermolecular distance from $R = 5.92$Å to $R = 5.69$Å. The small angle maximum occuring for $\Theta = 2.4°$ (Fig.1) and characteristic of the second coordination sphere of pure alcohol becomes visible only at a concentration of $X = 0.9$. Thus, it can be concluded that only at greater concentrations of alcohol in CCl_4 *i.e.* for $X > 0.6$ the associates of alcohol molecules which play the most important role in the scattered radiation intensity distribution.

These facts testify to the presence of intermolecular interactions among CCl_4 and $(CH_3)_3CHOH$ molecules in the range of low concentrations i.e. for $X < 0.1$. In the concentration range from $X = 0.1$ to $X = 0.6$ there probably occur structural zones including aggregations of either CCl_4 or the alcohol molecules or molecules of both compounds together. Above $X = 0.6$ the alcohol associates have a greater influence on the diffraction picture. The small angle maximum for $X = 0.9$ indicates that CCl_4 molecules do not disturb the already formed structure of liquid 2-methyl-2-propanol.

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