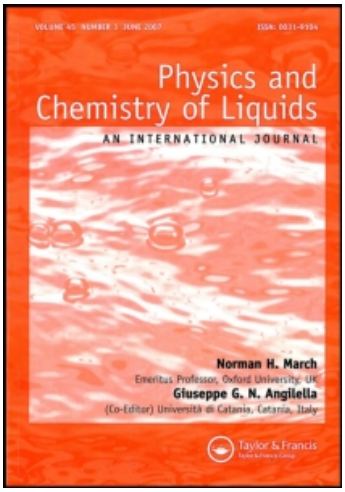

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X-RAY STUDIES OF 2-METHYL-2-PROPANOL SOLUTION IN CYCLOHEXANE

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Changes in the mean least intermolecular distances in a solution of 2-methyl-2-propanol in cyclohexane with increasing concentration of the former were found to be non-linear. Both in the range of low (0.005–0.04 molar fraction) and high (0.45–0.75 molar fraction) concentrations of the solutions studied local maxima of the mean least intermolecular distance were observed. In the range from 0.8 to 1 molar fraction the value of this parameter remained constant. Results obtained in this work prove the absence of the specific structural properties of a low concentration alcohol solution observed in other solvents. The occurrence of the local maxima proves that cyclohexane is a non-active solvent. Owing to this the molecules of the solute and the solvent assume positions ensuring homogeneity of the solvents.

Keywords: X-ray diffraction; intermolecular interactions; intermolecular distances

1. INTRODUCTION

Earlier dielectric studies of 2-methyl-2-propanol solutions in cyclohexane [1, 2] have shown anomalous changes of dielectric saturation as a function of concentration. Moreover, the same solutions revealed anomalous changes in density as a function of concentration relative to the corresponding changes obtained for the solutions of *n*- and sec-butanol in the same solvent [3]. This paper, on 2-methyl-2-propanol solutions in cyclohexane is a continuation of X-ray studies of alcohol solutions in carbon tetrachloride [4].

The character of changes in the mean least intermolecular distances R in solutions of 2-methyl-2-propanol in cyclohexane was studied by the X-ray diffraction method in a wide concentration range. The values R were obtained directly from the experimental curve of the scattered radiation intensity $I(eu)/N$, in electron units per unit of composition. We used the formula [5]: $R = 7.73/s_{max} - 0.3$, where $s = 4\pi \sin \Theta/\lambda$, λ is the wave length, and 2Θ is the scattering angle.

2. EXPERIMENTAL

Intensity of radiation scattered by a layer of the studied solution was determined by the transmission method using a typical X-ray diffractometer adapted for measurements of liquids. 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 2-methyl-2propanol and of cyclohexane used as a solvent were twice distilled. The value of molar concentration and molar mass for pure cyclohexane solutions of 2-methyl-2-proponal and pure alcohol are given in Table I.

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 cyclohexane and for pure cyclohexane, Table II.

In the angular distributions of the scattered radiation intensity, see Figure 1, the position of the main maximum is gradually shifted while the side maxima, typical of pure cyclohexane, at the concentrations of $X = 0.005$ and $X = 0.01$ molar fraction remain. The low-angle maximum characteristic of pure alcohol, for $\Theta = 2.4°$ is noticeable down to the concentration of $X = 0.7$ molar fraction and its trace is visible against the original beam even at $X = 0.4$ molar fraction.

The concentration dependence of the mean least intermolecular distance is non-linear, which is evident from Figure 2. It takes a maximum of 5.91 Å for the concentration of $X = 0.015$ molar fraction.

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

Formula of chemical compound	*Molar concentration X*	*Molar mass* $[10^{-3}\,Kg/Mol]$
$CH_2(CH_2)_4CH_2$	0.000	84.1656
"$C_{5.99}H_{11.99}O_{0.005}$"	0.005	84.1154
"$C_{5.98}H_{11.98}O_{0.010}$"	0.010	84.0652
"$C_{5.97}H_{11.97}O_{0.015}$"	0.015	84.0150
"$C_{5.96}H_{11.96}O_{0.020}$"	0.020	83.9648
"$C_{5.94}H_{11.94}O_{0.030}$"	0.030	83.8644
"$C_{5.92}H_{11.92}O_{0.040}$"	0.040	83.7640
"$C_{5.9}H_{11.9}O_{0.050}$"	0.050	83.6636
"$C_{5.89}H_{11.89}O_{0.055}$"	0.055	83.6033
"$C_{5.88}H_{11.88}O_{0.060}$"	0.060	83.5632
"$C_{5.87}H_{11.87}O_{0.065}$"	0.065	83.5130
"$C_{5.86}H_{11.86}O_{0.070}$"	0.070	83.4628
"$C_{5.84}H_{11.84}O_{0.080}$"	0.080	83.3624
"$C_{5.8}H_{11.8}O_{0.100}$"	0.100	83.1616
"$C_{5.6}H_{11.6}O_{0.200}$"	0.200	82.1577
"$C_{5.4}H_{11.4}O_{0.300}$"	0.300	81.1537
"$C_{5.2}H_{11.2}O_{0.400}$"	0.400	80.1498
"$C_5H_{11}O_{0.500}$"	0.500	79.1458
"$C_{4.9}H_{10.9}O_{0.550}$"	0.550	78.6438
"$C_{4.8}H_{10.8}O_{0.600}$"	0.600	78.1418
"$C_{4.7}H_{10.7}O_{0.650}$"	0.650	77.6434
"$C_{4.6}H_{10.6}O_{0.700}$"	0.700	77.1379
"$C_{4.4}H_{10.4}O_{0.800}$"	0.800	76.1339
$(CH_3)_3COH$	1.000	74.1260

Then, with increasing concentration this parameter rapidly decreases and starting from $X=0.04$ its decrease becomes slower. Then again R increases starting from $X=0.4$ and reaches a local maximum for X between 0.55 and 0.65. At the concentration $X=0.8$ molar fraction the mean least intermolecular distance assumes the lowest value of 5.69 Å, which is observed in pure alcohol.

4. DISCUSSION AND CONCLUSIONS

The concentration changes in the mean least intermolecular distance R for solutions of 2-methyl-2-propanol in cyclohexane, Figure 2 are different from those observed for the same solute in carbon tetrachloride, Figure 2 [4]. According to the earlier X-ray data, cyclohexane molecules are rather densely packed even at a room temperature [6].

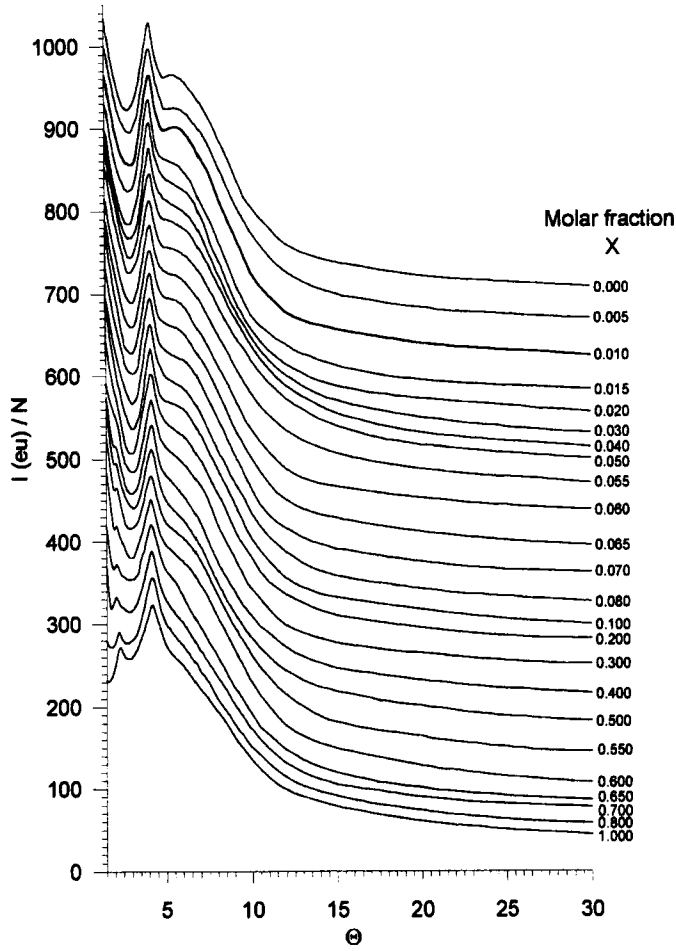

FIGURE 1 Mean angular distributions of the scattered radiation intensity for pure 2-methyl-2-propanol, $X = 1.000$, for alcohol solution in cyclohexane and for pure cyclohexane.

This packing is disturbed by an introduction of very small amounts of alcohol. Already at the alcohol concentration of $X = 0.015$ molar fraction, when there are about $n = 66$ cyclohexane molecules per a single alcohol molecule, Figure 3, the angular distribution of scattered radiation reveals changes, see Figure 1. The side maximum for $\Theta = 5.6°$ is not as clearly marked as for pure cyclohexane, and R takes

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* $R \pm 0.04$[Å]
0.000	4.095	5.82
0.005	4.087	5.83
0.010	4.080	5.84
0.015	4.040	5.91
0.020	4.067	5.86
0.030	4.070	5.85
0.040	4.090	5.83
0.050	4.090	5.83
0.055	4.092	5.82
0.060	4.100	5.81
0.065	4.097	5.82
0.070	4.100	5.81
0.080	4.100	5.81
0.100	4.105	5.80
0.200	4.130	5.77
0.300	4.145	5.75
0.400	4.160	5.72
0.500	4.145	5.75
0.550	4.110	5.80
0.600	4.110	5.80
0.650	4.130	5.78
0.700	4.140	5.76
0.800	4.185	5.69
1.000	4.185	5.69

a maximum value. With increasing alcohol concentration for $0.015 < X < 0.4$, the value of R decreases. This fact can be explained assuming that the components of the solution arrange into a specific packing realised thanks to their particular steric conditions. Cyclohexane molecules whose shape resembles a bath-tub at room temperature [6] can stick to the molecules of alcohol which are approximately spherical in shape [7]. The local maximum of R for $0.4 < X < 0.8$ molar fraction, Figure 2, is related to the anomalous changes in the density of the solution which takes a broad minimum in this concentration range [3].

Starting from the alcohol concentration $X > 0.4$ molar fraction the molecules of cyclohexane cease to have a significant effect on the ordering of the alcohol molecules, which is indicated by the character of the angular distribution of the scattered radiation intensity $I(\Theta)$, Figure 1, where a trace of the low-angle maximum characteristic of

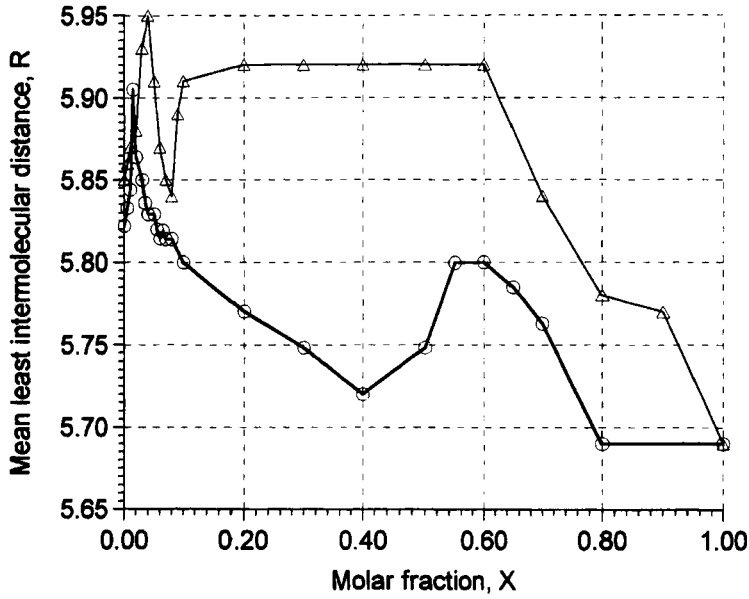

FIGURE 2 The values of the mean least intermolecular distance for various molar concentrations of 2-methyl-2-propanol in cyclohexane: ○○○ and carbon tetrachloride: △△△ [4].

pure 2-methyl-2-propanol [7] can be still discerned. In solutions of $X > 0.4$, the main role is played by the hydrogen bonds between the alcohol molecules [6]. Each molecule of the alcohol taking part in the hydrogen bond may have $n < 1.5$ neighbouring cyclohexane molecules, see Figure 3.

A comparison of the course of the "○○○" and "△△△" curves in Figure 2 indicates that the mean least intermolecular distance R in the solution studied strongly depends on the nature of interaction among the molecules of the pure components and on those among the solute and solvent. The local minimum of R observed in the solution of the same alcohol in CCl_4 [8] is a consequence of specific interactions among in CCl_4 molecules. In cyclohexane solution such a minimum does not occur as cyclohexane molecules do not show specific interactions. Therefore, even a very low concentration of the alcohol in cyclohexane results in a rapid increase in the mean least intermolecular distance R. For the concentrations $X > 0.4$, where

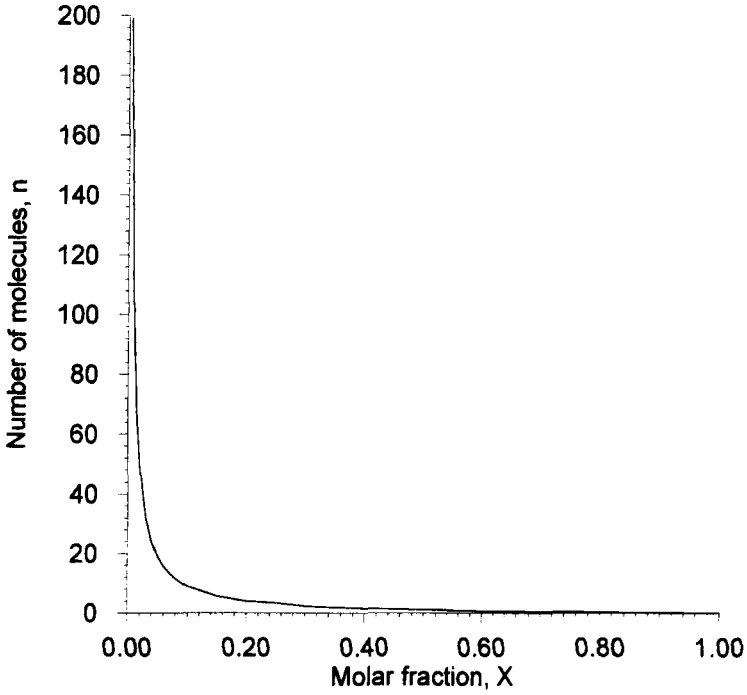

FIGURE 3 The number of cyclohexane molecules per a single molecule of 2-methyl-2-propanol as a function of concentration of the latter.

there are $n < 2$ cyclohexane molecules per a molecule of the alcohol, Figure 3, the ordering in the solution is close to that in pure 2-methyl-2-proponal [7]. Starting from the concentration $X = 0.8$ molar fraction the intermolecular distance R is the same as in pure alcohol.

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References

[1] Danielewicz-Ferchmin, I. (1968). *Bull. Acad. Polon. Sci. Cl. III*, **16**, 965.
[2] Danielewicz-Ferchmin, I. (1978). *Z. Phys. Chemie.*, **259**, 33.
[3] Danielewicz-Ferchmin, I. (1973). *Fiz. Diel. Rad.*, **6/2**, 205, Poznań, Poland.
[4] Mikusińska-Planner, A. (1997). *Phys. Chem. Liq.*, **35**, 87.

[5] Voigtlaender-Tetzner (1958). *Z. Phys.*, **150**, 215.
[6] Skryshevskii, A. F. (1980). Strukturnyy Analiz Zhidkostey and Amorfnykh Tel, Moskva: Izd. Vysshaya Shkola.
[7] Mikusińska-Planner, A. (1983). *Acta Cryst.*, **B39**, 394.
[8] Lawrence, J., Lowden, J. and Chandler, D. (1974). *J. Chem. Phys.*, **61**, 5228.