X-ray Structural Analysis of Liquid Solutions of *n*-Butanol-1 in Cyclohexane

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Angular distributions of intensity of X-ray radiation scattered in solutions of *n*-butanol-1 in cyclohexane have been measured and analyzed. The mean least intermolecular distances in the solution were determined. It was established that in the range of very low concentrations X of the solutions studied the distribution of the intermolecular distances $R(X)$ revealed three extremes. In this concentration range the fluctuations of the distance R are related to the earlier observed fluctuations of the solution density: the minimum in $R(X)$ at $X \cong 0.028$ mole fraction corresponds to the maximum in $d(X)$ in the range $0.015 \leq X \leq 0.035$ mole fraction, while the two maxima in $R(X)$ at $X \cong 0.007$ and $X \cong 0.05$ mole fraction correspond to the minima in $d(X)$ in the mole fraction ranges $0 \leq X \leq 0.015$ and $0.026 \leq X \leq 0.05$.

In the range $0.05 < X \leq 0.9$ mole fraction the main role in ordering of the solution molecules is played by the associated molecules of the alcohol with voids containing individual molecules of the solvent.

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

1. INTRODUCTION

Solutions of *n*-butanol-1 in cyclohexane have been already studied by IR absorption [1] and by dielectric methods [2]. Water solutions of this alcohol have been also studied, mainly by thermodynamic and spectroscopic methods [3–7]. The results explained certain thermodynamical properties and volume effects of these solutions in the low-concentration range. Structural information on these solutions following from the results of these studies have been indirect only.

The results of this study supplement the earlier X-ray investigation of water solutions of *n*-butanol-1 [8] and are expected to bring interesting new information since cyclohexane used as a solvent is inert relative to water.

Interpretation of the diffraction patterns is based on determination of the angular position of the main maxima Θ_{max} in the intensity of scattered radiation and calculation of the mean least distance between the centres of the scattering molecules from the formula [9]:

$$R = 7.73/s_{max} - 0.3. \qquad (1)$$

where: $s = 4\pi\sin\Theta_{max}/\lambda$ depends on the angle of scattering 2Θ and length λ of X-ray radiation.

2. EXPERIMENTAL

X-ray diffraction patterns were recorded using a typical X-ray diffractometer equipped with a specially designed and constructed cell for measurements of liquids. The samples studied were liquid layers of 1 mm in thickness confined by windows made of mica. The cell was placed between the source of monochromatic radiation $MoK\alpha$ and the counter probe. Pure *n*-butanol-1 was obtained by recrystallisation from analytically pure alcohol and cyclohexane was twice distilled. The solutions of *n*-butanol-1 in cyclohexane were studied in the whole range of concentrations at 293.15 K. Taking into regard the earlier noted specific structural effects in diluted solutions of the alcohol [10 – 13], a greater number of measurements were made in the range $0.005 \leq X \leq 0.06$ (X is the mole fraction of the alcohol). The values of molar concentrations, masses, angles Θ_{max} and intermolecular distances R are collected in Table I.

The molar masses of the solutions given in Table I were calculated from the equation:

$$M_{C_aH_bO_c} = a \cdot M_C + b \cdot M_H + c \cdot M_O, \qquad (2)$$

where: $a, b, c = \sum_{i=1}^{k} x_i \cdot n_i$, and x_i is the mole contribution of the *i*-th molecule of the solution, n – the number of atoms of a particular kind in the *i*-th molecule.

TABLE I Molar concentrations, masses, angles Θ_{max} and mean least intermolecular distances for the solutions studied and pure components of the solutions

No.	Molar concentration X	Molar mass M $[10^{-3}$ kg/mol]	Position of the maxima Θ_{max} [°]	Mean least intermolecular distances $R \pm 0.04$ [Å]
1	0	84.1656	4.095	5.82
2	0.005	84.0434	4.085	5.84
3	0.010	84.0652	4.100	5.81
4	0.015	84.0150	4.110	5.80
5	0.020	83.9648	4.135	5.76
6	0.025	83.9146	4.140	5.75
7	0.030	83.8644	4.160	5.72
8	0.035	83.8142	4.130	5.77
9	0.040	83.7640	4.105	5.80
10	0.045	83.7138	4.100	5.81
11	0.050	83.6636	4.075	5.85
12	0.055	83.6033	4.085	5.84
13	0.060	83.5632	4.125	5.78
14	0.080	83.3624	4.135	5.76
15	0.200	82.1577	4.175	5.70
16	0.400	80.1497	4.230	5.63
17	0.500	79.1458	4.260	5.58
18	0.600	78.1418	4.350	5.46
19	0.700	77.1379	4.405	5.39
20	0.800	76.1339	4.510	5.26
21	0.900	75.1299	4.525	5.24
22	1	74.1260	4.540	5.22

3. RESULTS

The obtained angular distributions of the intensity of radiation scattered by the samples studied are presented in Figure 1. The intensity distributions I_{eu}/N are normalised to the electron units (eu), with regard to the theoretical curve (one of them is presented as the
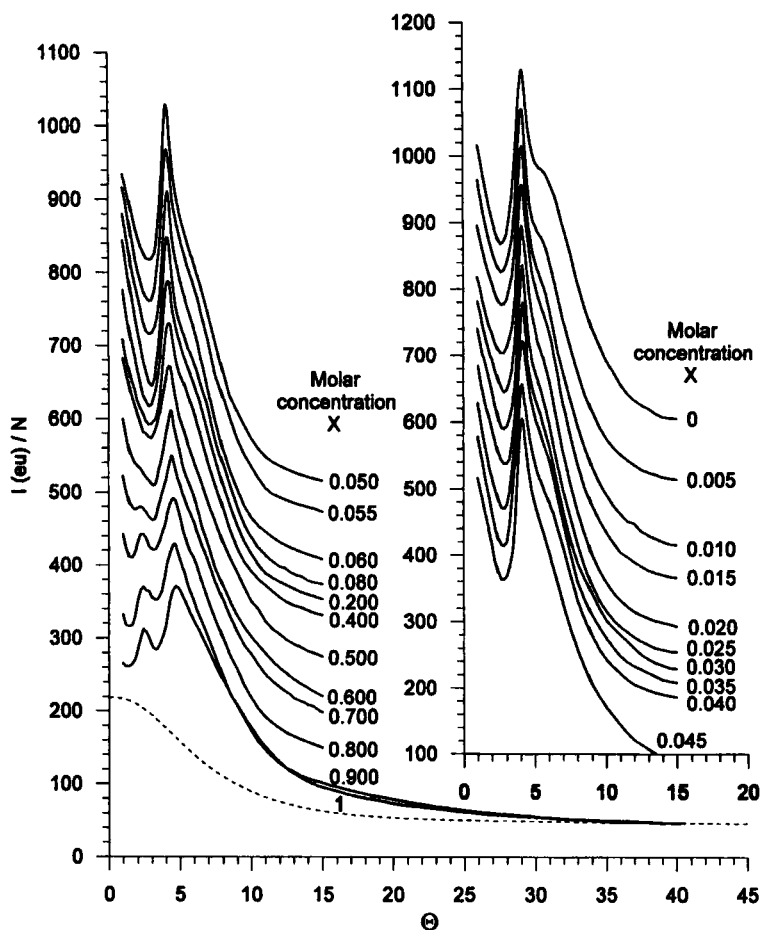
FIGURE 1 Mean angular distribution of the scattered radiation intensity for pure cyclohexane, $X = 0$, for alcohol solution in cyclohexane $0.005 \leq X \leq 0.9$ and for pure n-butanol-1, $X = 1$.

broken line in Fig. 1). The theoretical grounds for normalisation of the experimental curve are given in [14].

The angular positions of the main maxima of the scattered radiation intensity curves and the corresponding intermolecular distances R, calculated from formula (1), are given in Table I. The value $R = 5.22 \pm 0.04 \text{Å}$ obtained for pure n-butanol-1, Table I, is in good agreement with the earlier determined radii of the molecule $R = 2.64 \text{Å}$ and $R = 2.4 \text{Å}$ [15], whose values indicate a little deviation from the spherical symmetry. The value $R = 5.82 \text{Å}$, obtained for cyclohexane is in good agreement with that reported in [17].

The dependence of the mean least intermolecular distances R on the solution concentration X is shown in Figure 2. As follows from the figure, this dependence is not linear.

In the range of low concentrations, up to $X = 0.06$ mole fraction, the distance R takes extreme values for $X = 0.005$, $X = 0.03$ and $X = 0.05$, (Fig. 2, Tab. I). At $X = 0.005$ mole fraction, a small increase in the
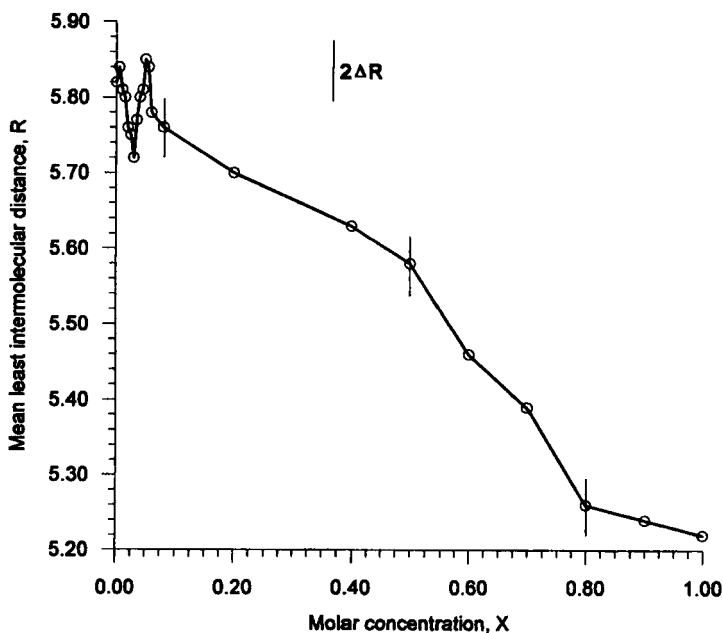

FIGURE 2 The values of the mean least intermolecular distances R for various molar concentration of n-butanol-1 in cyclohexane.

intermolecular distance R is observed relative to its value in pure cyclohexane. With a further increase in the concentration X, the distance R decreases, reaching $R = 5.72\,\text{Å}$ for $X = 0.03$. For a further increase in X, the value of R increases reaching a maximum of $R = 5.85\,\text{Å}$, for $X = 0.05$, and then R rapidly decreases to $R = 5.78\,\text{Å}$ for $X = 0.06$. In the ranges: $0.06 \leq X \leq 0.5$, $0.5 < X \leq 0.8$ and $0.8 < X \leq 1$ the changes in R are approximately linear.

4. DISCUSSION AND CONCLUSIONS

The character of $R(X)$ in the range of low concentrations, Figure 2, indicates a disturbance in the distribution of cyclohexane molecules caused by the introduction of n-butanol-1 molecules. The observed fluctuations of the intermolecular distances R, in the range of very low concentrations are most probably related to the changes in the solutions densities. Similar fluctuations in the density of the same solutions and in the same range of low concentrations have been observed earlier [16]. Figure 3 shows a comparison of the two curves $R(X)$ and $d(X)$ for the same solutions, obtained at $T = 293.15\,\text{K}$.

As follows from the figure the changes in these two parameters R and d are correlated. The local minimum in $R(X)$ observed at $X \cong 0.028$ correlates with the local maximum in density $d(X)$ observed at $X \cong 0.025$. The local maxima in $R(X)$ at $X \cong 0.007$ and $X \cong 0.05$, correlate with the local minima in $d(X)$ at $X \cong 0.008$ and $X \cong 0.04$. The similar characters of these dependencies prove a direct relation between the changes in density and intermolecular distance.

The character of $R(X)$ changes, especially in the range of low concentrations, determined for n-butanol-1 solutions in water (an active solvent) is completely different. In water solutions, with increasing concentration of n-butanol-1 the intermolecular distance continuously increases Figure 4 [8], except in the range $0.005 \leq X \leq 0.015$ where it is constant. This continuous increase in the intermolecular distance is related to the destruction of the water structure involving breaking of hydrogen bonds and the hydrogen bond type interactions between the molecules of the two components of the solution [8].
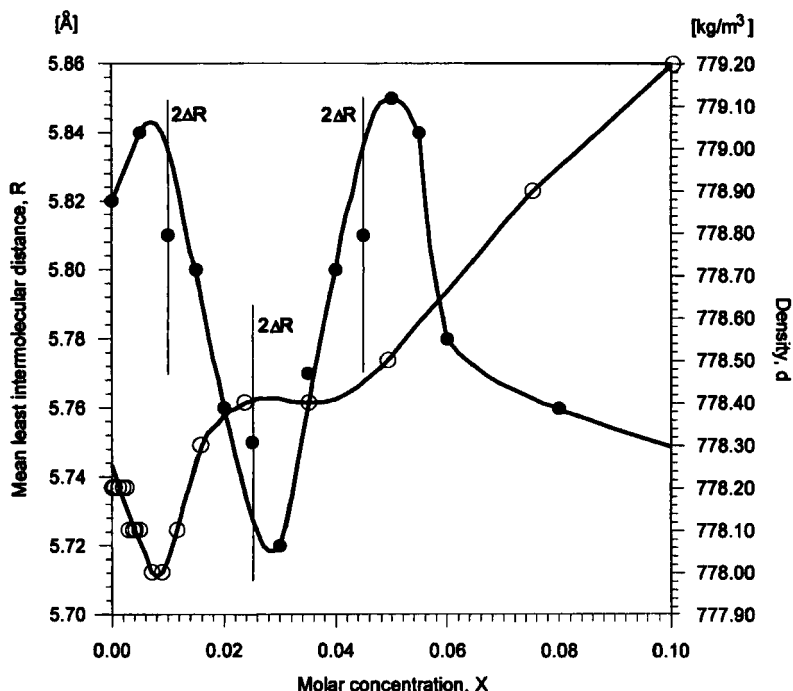
FIGURE 3   The intermolecular distance R(•-•-•) and density d(o-o-o) [14] of the solutions of n-butanol-1 in cyclohexane *versus* the concentration of these solutions, at $T = 293.15\,K$.

   In the solutions of n-butanol-1 in cyclohexane the structure of the latter is not destroyed because it is inert. The introduction of n-butanol-1 molecules causes only a displacement of its molecules. Moreover, the diameter of the two kinds of molecules is similar: $5.82\,\text{Å} \cong 5.22\,\text{Å}$ (Tab. I). Therefore, relative changes in R are much smaller than those observed in the water solutions of n-butanol-1, in n-butanol-1 solution in cyclohexane the relative change in R is $R_{max}/R_{min} = 0.60$, while in water $-R_{max}/R_{min} = 2.18$ [8]. That is why in this work the error $\Delta R = \pm\,0.04\,\text{Å}$ (Fig. 3) makes as much as 6.5% relative changes in R, while in the water solutions this error is barely 2% because water molecules are much smaller than those of the alcohol; $3.11\,\text{Å} < 5.22\,\text{Å}$. The error ΔR, as shown in Figure 3, is only apparently great because the changes in R are small as the diameters of the two kinds of molecules are similar.
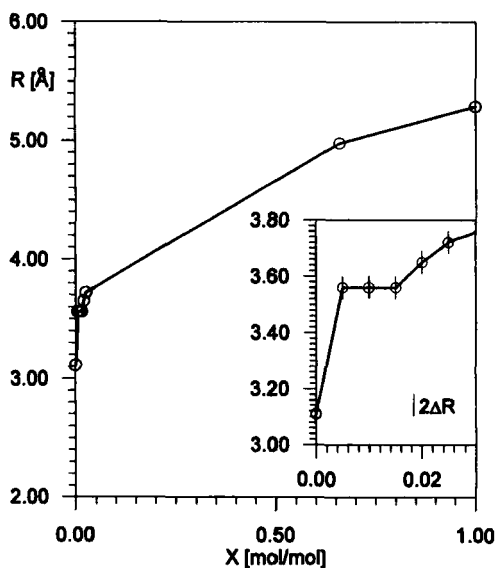
FIGURE 4 The values of the mean least intermolecular distance for various molar concentrations of n-butanol-1 in water [8].

In the range of low concentrations, $X < 0.06$, there are many more molecules of cyclohexane than of n-butanol-1. At the concentrations $X = 0.005$, 0.03 and 0.05, there are about 200, 30 and 20 solvent molecules per one molecule of the alcohol, respectively [17]. At the concentration of $X \approx 0.005$, individual non-associated molecules of the alcohol [1] penetrate among greater molecules of the solvent. They can cause a displacement of the latter leading to an increase in R, but on the other hand, since they enter the voids among the molecules of cyclohexane they increase the packing leading to a decrease in R. As increasing concentration of the alcohol favours the association of its molecules [2], growing associates push aside the molecules of cyclo-hexane, which results in an increase in R up to $R = 5.85 \text{Å}$ at $X = 0.05$. For $X > 0.05$, the value of R decreases. With decreasing R the molar volume of the solution decreases which means that the degree of association of n-butanol-1 molecules increases [2]. In the concentration range $0.05 < X \leq 0.9$ the ordering of the solution molecules is determined by the associated molecules of the alcohol, and then in the voids among them there are individual molecules of the solvent.

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