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X-Ray Diffraction Study of Mixing States in the Carbon Tetrachloride Solutions of Methanol and Pentane

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A simple method has been proposed for estimating the state of mixing in a binary solution directly from the radial distribution function. The method has been applied to the estimation of the size of the cluster or aggregate in a binary solution of methanol and carbon tetrachloride. Pure liquid carbon tetrachloride and a binary solution of pentane and carbon tetrachloride have also been studied as reference systems. The number of methanol molecules which form a cluster in the solution at the volume ratio of 8.5(CCl_4):1.5(CH_3OH) has been estimated to be about 18, which is in good agreement with an estimate by light scattering.

Many X-ray diffraction studies have been carried out to investigate molecular arrangements in liquids. However, the structure analysis for a molecular liquid, even if it is a pure liquid, is rather difficult. A structure cannot be uniquely determined by diffraction methods, since the packing of polyatomic molecules in the liquid is three-dimensional while the information on molecular geometry obtainable from a diffraction pattern is limited to only one dimension. Usually a structure model is constructed by comparing an intensity or radial distribution function calculated for a model with the experimental one. However, it is often difficult to find a model which can sufficiently explain the experimental facts. Even if a model which yields a calculated intensity in good agreement with the experimental one is obtained, there is no assurance that this model is unique. It is often the case that models which are different from one another in the sense of a three-dimensional arrangement give very similar scattering intensities.

For a multi-component organic solution, it becomes still more difficult to make a structure analysis, and very few studies have been carried out. One example is the work by Narten on a CCl_4–$C(CH_3)_4$ system.[1] He observed a radial distribution function only up to 10 Å and interpreted the radial distribution function of the mixture only as a superposition of the radial distribution functions corresponding to the components, CCl_4 and $C(CH_3)_4$. Therefore, his interpretation is only valid for those peaks due to intramolecular interferences or due to intermolecular interferences for the first nearest neighbors concerned. In the case of a mixture of molecular liquids, one should carefully consider the state of mixing, that is, how one component is mixed with the other components, or how molecules of one component are dispersed in molecules of the other components. As will be described in this paper, the information from the radial distribution function up to large distance is important for considering the state of mixing.

In this report we present a simple method by which we estimate the state of mixing in binary mixtures with carbon tetrachloride solvent directly from a radial distribution function. The existence of a long-range correlation in the observed radial distribution function for pure liquid CCl_4 has been well established.

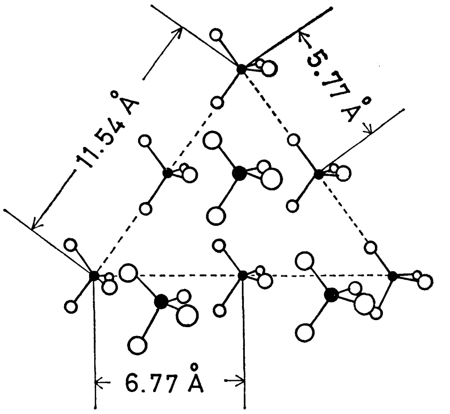


Fig. 1. Packing model for pure liquid CCl_4 (see Ref. 2).
Packing of adjacent molecules is head-tail head-tail with the molecular distance of 5.77 Å. We call this model a "bcc cluster model," because the three-dimensional packing results in a bcc lattice.

The structure of pure liquid CCl_4 has been investigated in detail and a reasonable local structural model has been proposed,[2,3] as shown in Fig. 1. The scattering intensity curve can supply suitable information for the destruction of this long-range structure of liquid CCl_4 by the addition of the other components.

In order to obtain information about the state of mixing, we carried out an X-ray diffraction experiment. Two kinds of carbon tetrachloride solutions, CCl_4–CH_3OH and CCl_4–n-C_5H_{12} systems, were chosen for the samples. In a CCl_4–CH_3OH system, methanol molecules are expected to form clusters through strong hydrogen-bonding. This expectation has been supported by the observed entropy change on mixing,[4] the magnitude of the concentration fluctuation observed by a light scattering experiment, and by theoretical interpretations.[5–7] For a CCl_4–n-C_5H_{12} system, on the other hand, a state of random mixing is believed to be realized.[8,9] It has been reported for the binary solution of methanol and carbon tetrachloride that the fluctuation of concentration has a maximum value at the molar ratio of 7.0(CCl_4):3.0(CH_3OH). It is expected that the aggregate number of methanol molecules becomes maximum at this concentration. Therefore, we observed the diffraction intensity at the corresponding volume ratio of 8.5(CCl_4): 1.5(solute) for the CCl_4–CH_3OH and CCl_4–n-C_5H_{12} systems.

In these systems, it is important that the scattering intensities of the X-rays for the solute molecules, methanol and pentane, are negligibly weak in comparison with that for the solvent molecule, carbon tetrachloride.

Experimental

The scattering intensities of X-rays from liquid samples were measured at 25 °C. An energy-dispersive diffractometer with a vertical goniometer (θ-2θ scanning system) was used.[10] A fine-focus X-ray tube with a tungsten target was used at 45 kV and 20 mA. The scattering intensity was recorded by a multi-channel pulse-height analyzer connected with a Si(Li)-detector. The scattering intensity was measured by the transmission method at scattering angles, 2θ, of 2.5, 4.0, 7.0, 12.0, 20.0, and 35.0°.

The sample holder was the same as that used previously.[11] In the present study, windows of Mylar film (20 μm) were used. The specimens used in this experiment were of commercially available reagent grade. Carbon tetrachloride and pentane were used without further purification. Methanol was further purified by a single distillation.

Data Analysis

The observed scattering intensity was smoothed and was corrected for the scattering from the windows. The scattering intensity curve, thus obtained, was normalized to the energy-distribution curve of the incident beam. The absorption correction was also made by the use of calculated absorption coefficients.[12] The corrected intensity curve was then converted to an absolute scale (in the electron unit) by fitting the experimental intensity to the theoretical one at large s-values. For a pure liquid, the theoretical intensity may be estimated from the intensity calculated for one free molecule. In the case of a binary mixture, the theoretical intensity is a superposition of the scattering intensities from the two components. However, as the scattering intensities from CH_3OH and n-C_5H_{12} are negligibly weak in comparison with that from CCl_4, the theoretical intensity at large s-values may be obtained from the intensity calculated for carbon tetrachloride only. This corresponds to the treatment in which a CCl_4 molecule is fixed as a central molecule and the radial distribution function is regarded as the distribution of other molecules (CCl_4 molecules or solute molecules) around the central molecule. This treatment excludes the case in which a solute molecule occupies the position of the central molecule in the radial distribution function. In the calculation of the scattering intensity for a free CCl_4 molecule, the internuclear distances and the mean-square amplitudes of vabration for CCl_4 obtained by gas electron diffraction[13] were used. The Compton scattering intensity calculated by Cromer was subtracted.[14] The total coherent intensity thus obtained is

$$I_{co}(s) = \sum_n f_n(s)^2 + i_1(s) + i_2(s), \tag{1}$$

where $f_n(s)$ is the atomic scattering factor, $i_1(s)$ is the coherent intensity from atomic pairs belonging to a CCl_4 molecule, $i_2(s)$ is the coherent intensity from atomic pairs belonging to different CCl_4 molecules.

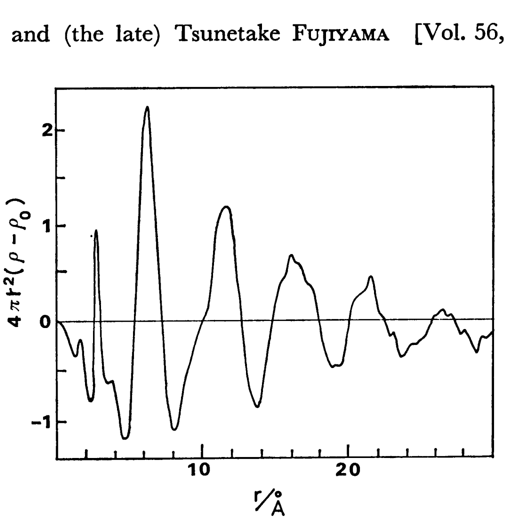


Fig. 2. Radial distribution function observed for liquid CCl_4 at room temperature.

The electron radial distribution function from which the bulk density was subtracted, $4\pi r^2(\rho(r)-\rho_0)$, was obtained by the Fourier transformation of $si(s)$ which is defined by $si(s)=s(i_1(s)+i_2(s))$,

$$4\pi r^2(\rho(r)-\rho_0) = \{2r/(\pi \sum_n Z_n^2)\} \sum si(s)\cdot\sin(sr)\Delta s, \tag{2}$$

where ρ_0 is the bulk liquid density of CCl_4 in the mixture and Z_n is the atomic number of the n-th atom of a CCl_4 molecule.

In the energy-dispersive method, the scattering intensity is scarcely influenced by the fluctuation in the incident beam intensity. Therefore, the accuracy of the observed intensity is mainly limited to the statistical random error, which is estimated to be about 0.5% of the total intensity. The error of scaling due to the neglect of the scattering intensity of the solute molecule is less than 1% in the s-region used for the scaling.

Results and Discussion

The electronic radial distribution functions observed for pure liquid CCl_4,[10] CCl_4–n-C_5H_{12}, and CCl_4–CH_3OH are shown in Figs. 2, 3, and 4, respectively. It can be seen from these figures that, in the case of the CCl_4–CH_3OH system, the peaks occuring at r-values larger than 18 Å are smeared out. On the other hand, there exists clear structure correlation in the mixture of CCl_4–n-C_5H_{12} up to values as large as those observed in the pure liquid CCl_4.

Radial Distribution Function of a Solution with "Vacancies." As described in the introduction, the scattering power of X-rays from solute molecules, methanol or pentane, is negligibly weak in comparison with that from carbon tetrachloride. Therefore, in the first approximation the scattering from these binary systems can be analyzed as though the CCl_4 liquid had "vacancies" whose volumes are equal to those of solute molecules or clusters of the solute molecules. This "vacancy" does not mean that a real void exists in the liquid, but that the scattering power of X-rays by a solute molecule or a cluster can be disregarded.

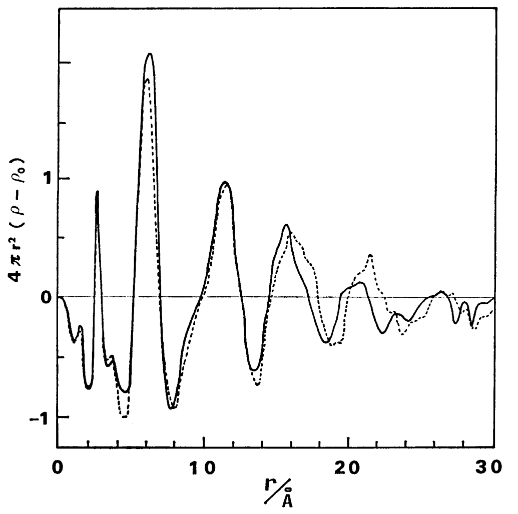


Fig. 3. Radial distribution functions for a binary solution of CCl$_4$ and n-C$_5$H$_{12}$. (——): Observed, (······): calculated for "ideal mixing."

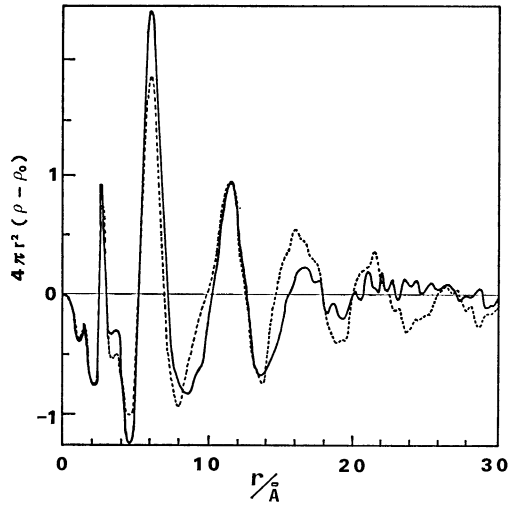


Fig. 4. Radial distribution functions for a binary solution of CCl$_4$ and CH$_3$OH. (——): Observed, (······): calculated for "ideal mixing."

Hereafter in this paper, the term "vacancy" is used in this sense. The analysis of the radial distribution function observed in the binary solutions can be replaced by the analysis of the "vacancy" distribution in liquid CCl$_4$. In the analysis of the mixing state of such solutions, the following assumptions were made:

(a) It is possible to neglect the scattering intensity of X-rays from solute molecules.

(b) On passing from a pure liquid to the solution, the structure of the solvent is not influenced by the solute molecules.

The error caused by the assumption (a) is estimated to be 5% in the radial distribution function. Namely, the radial distribution functions with "vacancies" in place of the solute molecules are estimated to be 5% smaller in amplitude than the real radial distributions shown by the solid curves in Figs. 3 and 4 containing the contribution of scattering power of solute molecules. This situation, however, does not affect the following discussion. The assumption (b) means that an integral number of sites or CCl$_4$ molecules is replaced by non-scattering solute molecules ("vacancy") without distortion of the distribution of the sites, namely, the positions which would be occupied by CCl$_4$ molecules if the system were pure CCl$_4$ liquid. So the volume of the "vacancy" is assumed to be an integral multiple of the volume of a CCl$_4$ molecule. Under those assumptions, we will consider the relation between the state of mixing in a binary solution and the radial distribution function.

The radial distribution curve of liquid CCl$_4$ shows several peaks up to $r \simeq 28$ Å (Fig. 2). By looking at these peaks we may say that a certain number of molecules are located around a representative central molecule at a certain distance from it, if we ignore complications arising from the fact that the molecules are polyatomic and have structure and orientation. In other words, if we sat on the representative central molecule and looked around, we would see several sites that are occupied by other molecules. As is described in the analysis, the data are scaled in such a way that the central molecule is always a CCl$_4$ molecule and never a "vacancy."

The peak height of the radial distribution curve at a distance r is proportional to the time-averaged number of molecules which occupy the sites at a distance r from the central molecule. Because of the isotropy of the liquid, it is only necessary to consider one representative site instead of all the sites which are located at a given distance from the central molecule.

In the case of the binary solutions discussed in the present paper, the site is not always occupied by another molecule, but is sometimes occupied by a "vacancy." As a result, the peak-height of the radial distribution function decreases in comparison with that of a pure liquid.

If we denote the maximum length between two points within the "vacancy" by $2R$, (which is equal to the diameter in the case of a spherical "vacancy"), it is shown in Appendix that

(i) For $r \geq 2R$, the peak-height decreases to $(1-\alpha)$ times that of the pure liquid where α is the volume fraction of the "vacancies."

(ii) For $r < 2R$, the extent of decrease is less than that for $r \geq 2R$.

Figures 2, 3, and 4 show the quantity $4\pi r^2(\rho(r)-\rho_0)$ instead of the radial distribution function, where ρ_0 is the value of $\rho(r)$ in the limiting case of $r \to \infty$. The term $-\rho_0$ appears because the Fourier transform of the interference term of the coherent intensity is computed without the central scattering (the scattering intensity at $2\theta = 0°$).[15] The value of ρ_0 for a binary solution is evidently $(1-\alpha)$ times that of the pure liquid. Thus the above statements (i) and (ii) are valid also for the curve of $4\pi r^2(\rho(r)-\rho_0)$.

Now, let us consider the distribution function of the binary solutions of carbon tetrachloride for two model cases.

1) The case where the size of a "vacancy" is nearly equal to that of CCl$_4$ molecule.

In this case, the size of the "vacancy" $2R$ is equal to the diameter of a CCl$_4$ molecule. Therefore, the

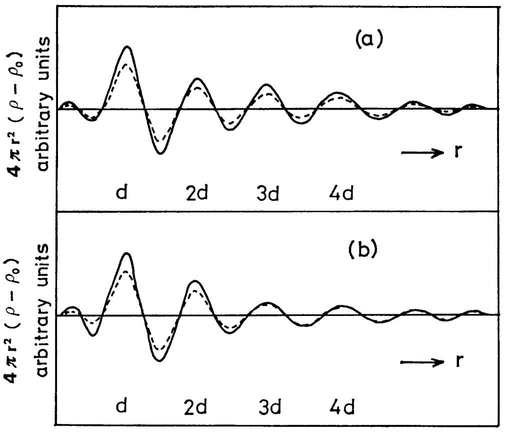


Fig. 5. Radial distribution functions expected for various mixing states for a model case of $\alpha \simeq 0.25$. (a) The case that the "vacancy" size is equal to that of a CCl_4 molecule. (——): Pure CCl_4, (----): ideal mixing. (b) The case that the "vacancy" size is three times as large as that of CCl_4 molecule. (——): Solution, (----) ideal mixing.

above statements (i) and (ii) predict that the distribution function in this case is reduced by a factor of $(1-\alpha)$ from that of the pure liquid for all the r-values exceeding the diameter of a CCl_4 molecule. In other words, all the peaks beyond that of the first nearest neighbors are reduced to $(1-\alpha)$ times those of the pure liquid. Hereafter, we call this case "ideal mixing." The distribution function in this case is schematically shown in Fig. 5(a), where α is tentatively assumed to be 0.25.

2) The case where the size of the "vacancy" is larger than that of a CCl_4 molecule.

As an example, we consider the case where the "vacancy" size $2R$ is three times as large as the diameter of CCl_4 molecule. The peak-heights of the distribution function, in this case, are considerably stronger than those of the "ideal mixing" case for peaks corresponding to $r<2R$, *i.e.*, the first and second nearest neighbors. For the peaks corresponding to larger r, the distribution function has essentially the same magnitude as that of the "ideal mixing" case, that is, $(1-\alpha)$ times those of the pure liquid. This situation is schematically visualized in Fig. 5(b).

We reach the conclusion that we can estimate the "vacancy" size directly from the observed distribution function. That is to say, the observed radial distribution function becomes equal to that of the "ideal mixing" case at $2R$, which corresponds to the maximum length of the "vacancy." The distribution curve of the "ideal mixing" case can be obtained as $(1-\alpha)$ times that for pure liquid CCl_4.

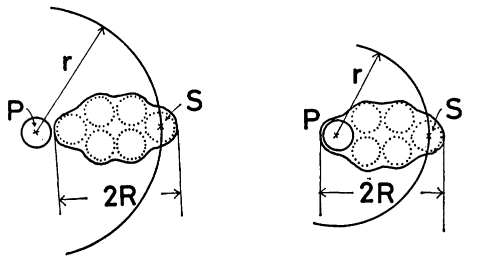
States of Mixing in CCl_4*–n-*C_5H_{12} *System.* The experimental radial distribution function, $4\pi r^2(\rho(r)-\rho_0)$, is shown in Fig. 3 (see the solid curve). A correlation as clear as that for pure liquid CCl_4 (see Fig. 2) is observed up to 27—28 Å. It is also seen that the peak heights of the distribution function are similar to those expected from "ideal mixing," *i.e.*, those obtained by multiplying the distribution function of pure liquid CCl_4 of Fig. 2 by $(1-\alpha)$. The important feature of the distribution curve for CCl_4–*n*-C_5H_{12} is that the intensity reduction, $(1-\alpha)$, on passing from pure liquid to the solution is nearly equal at any distance r, which corresponds to the situation drawn in Fig. 5(a). This suggests that the state of mixing in the CCl_4–*n*-C_5H_{12} is "ideal." Since the sizes of the solute and solvent molecules are almost the same, *n*-C_5H_{12} molecules are randomly dispersed in CCl_4 liquid without forming clusters.

States of Mixing in CCl_4*–*CH_3OH *System.* The experimental radial distribution function is shown in Fig. 4 by the solid line, while the distribution function expected for "ideal mixing" is illustrated by a broken line. The magnitude of the former curve is larger than that of the latter at the first peak at 6.3 Å, and these two curves are nearly equal at 12 Å. The peak at 6.3 Å observed for pure liquid CCl_4 has been assigned to the superposition of the first nearest correlations at 5.77 and 6.77 Å (see Fig. 1). The peak at about 12 Å corresponds mainly to the interference at (2×5.77) Å, although it is superimposed on other interferences. On the whole, the behavior of the observed distribution function relative to the "ideal mixing" is similar to that of Fig. 5(b).

The fact that the height of the two curves coincide at 12 Å indicates that the diameter of the methanol cluster is about 12 Å, if the form of the cluster is assumed to be nearly spherical. Since the diameter of a CCl_4 molecule is about 6 Å, the cluster volume is estimated to be about eight times as large as that of a CCl_4 molecule. As the molecular volumes of carbon tetrachloride and methanol at room temperature are 153 and 66.4 Å^3 respectively, the number of methanol molecules which form a cluster is estimated to be $153\times8/66.4\simeq18$. This conclusion is in good agreement with that from the light scattering experiment,$^{6)}$ which found that the cluster formed in the CCl_4–CH_3OH system at 0.3 mole fraction was composed of about 17 molecules.

In the experimental radial distribution curve shown in Fig. 4, the observed peaks at larger r-values become broader and weaker in comparison with those of "ideal mixing." This deviation of the observed distribution function from that of the "ideal mixing" case at r-values longer than 16 Å may be ascribed to the modification of the long-range structure of liquid CCl_4 caused by the existence of the solute molecules. A detailed analysis of this effect is left for a future problem.

In summary, the distribution functions observed for CCl_4 solutions can be explained by the use of a simple model. This result, in turn, supports the validity and the usefulness of the model for the elucidation of the state of mixing in a binary solution. The present study demonstrates that X-ray diffraction can be used to study the state of mixing in solution without recourse to small-angle-scattering, when the solution contains two kinds of molecules and one component has a much larger scattering power than that of the other component.



(a) (b)

Fig. 6. Particular arrangements of a representative central molecule and a "vacancy". Small circle is a central molecule. The dotted circles are the sites replaced by a "vacancy." (a) The case of $r \geq 2R$ and (b) the case of $r < 2R$. See Appendix for details.

Appendix

Derivation of Statements (i) and (ii) in the Text about the Peak Heights of the Radial Distribution Curve of Binary Solutions.

In the following discussion, it is assumed that an integral number of sites or CCl_4 molecules are replaced by "vacanices" and that the structure or the distribution of the sites are not distorted even if some of the sites are occupied by "vacancies." The radial distribution function shows the time-averaged number of molecules which occupy the site at a distance r from a molecule, which is defined as a representative central molecule. In Fig. 6 are shown a representative central molecule P in a binary solution, a site S located at a distance r from P, and a "vacancy" in a particular orientation. In the treatment of this paper (see Data Analysis), the central site P is always occupied by a CCl_4 molecule.

(A) As long as the distance between S and P is equal to or larger than the effective size of the "vacancy" $2R$, any dotted circle in the vacancy can occupy the site S and all possible orientations of the "vacancy" are permitted. Even if the "vacancy" is orientated in such a way as shown in Fig. 6(a), where the "vacancy" is in contact with the central molecule P, this orientation is still permissible. Therefore, the fraction that the site is occupied by a "vacancy" is simply the volume fraction α, and the time-averaged number of CCl_4 molecules which occupy the site S is $(1-\alpha)$ times that of pure liquid CCl_4. This factor leads to the factor $(1-\alpha)$ for the decreasing factor of the peak height in the case $r \geq 2R$.

(B) If the site S is located at r which is less than $2R$, it happens that some of the orientations of a "vacancy" which occupies the site S should be excluded in counting the fraction that the site is occupied by a "vacancy." In Fig. 6(b), one such orientation is shown. This arrangement should be excluded, because in this orientation the central molecule has also to be replaced by the "vacancy," in contradiction to the initial assumption. Accordingly, the fraction that the site S is occupied by a "vacancy" is less, and the fraction that the site S is occupied by a CCl_4 molecule is more, than that of the case in (A). So the peak height is larger than that of the case in (A).

As is described above, the peak height of the radial distribution curve at a distance r is proportional to the time-averaged number of molecules which occupy the sites at a distance r from a representative central molecule. On the other hand, we may also say that the peak height of the radial distribution curve is proportional to the space-averaged number of molecules which can find a site at a distance r from them occupied by another molecule. This is a space-averaged picture of the problem in contrast to the time-averaged picture mentioned in the preceding. In the following, the statements (i) and (ii) described in the text will be derived on the basis of the space-averaged picture of the problem.

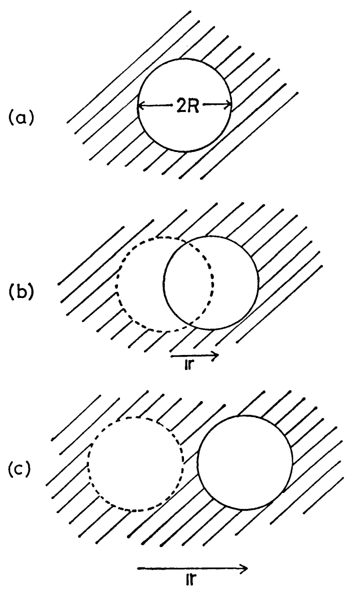


Fig. 7. The space-averaged picture.
(a) A part of the binary solution. A vacant space is a solute molecule or a cluster of them. The diameter of the space is $2R$. (b) The solid circle is the "vacancy." The dotted circle is the "image" obtained by shifting by $\boldsymbol{r}$, in the case of $r < 2R$. (c) In the case of $r \geq 2R$.

According to the assumption of the present work, the radial distribution function is that of pure liquid CCl_4 multiplied by the probability that a site at a distance r from molecule of carbon tetrachloride is found outside the "vacancy," in other words, within the portion of the solution that is occupied by carbon tetrachloride. This probability is given by a characteristic function or a shape function of a figure[16] and can be evaluated as follows.

In Fig. 7(a) is depicted a part of the solution where a vacant space shows a solute molecule and the shaded portion is occupied by solvent molecules. Although there only one vacant space is shown in Fig. 7(a), the figure should extend almost infinitely containing an enormous number of vacant spaces, keeping their volume fraction equal to that of the solute molecules denoted by α.

We then draw an "image" of the figure by shifting the whole figure by a vector $\boldsymbol{r}$ as shown in Fig. 7(b). It is evident that only those molecules that are in the shaded region of Fig. 7(b) can find a site outside the vacant spaces at the position defined by the vector $\boldsymbol{r}$ from themselves. The ratio of the volume of the shaded region of Fig. 7(b) to that of Fig. 7(a) gives the probability that a site at a distance r from a solvent molecule and in a particular direction defined by the vector $\boldsymbol{r}$ is found outside the vacant spaces.

The ratio gradually decreases as r becomes larger, but it remains constant for any orientaion of the "vacancy" if r exceeds $2R$, the maximum length between any two points in the "vacancy" (see Fig. 7(c)). The constant value of the ratio is $(1-2\alpha)/(1-\alpha) \simeq 1-\alpha$.

Because of the isotropy of the liquid, the foregoing argument is valid in any direction of the vector. Thus the probability that a site at a distance r from a solvent molecule is found outside the solute molecules decreases gradually from unity to $(1-\alpha)$ as r increases from 0 to $2R$, and remains constant, $(1-\alpha)$, in the region of r beyond $2R$.

In the present qualitative discussion, such a complication as overlapping of the image of a vacant space with another vacant space is ignored, since this effect should only modify the probability on the order of α^2.

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References

1) A. H. Narten, ORNL Rept. ORNL-4203 (1967).

2) K. Nishikawa and Y. Murata, *Bull. Chem. Soc. Jpn.*, **52**, 233 (1979).

3) K. Nishikawa, K. Tohji, M. Shima, and Y. Murata, *Chem. Phys. Lett.*, **64**, 154 (1979).

4) G. Scatchard and L. B. Tickner, *J. Am. Chem. Soc.*, **74**, 3274 (1952).

5) T. Fujiyama and M. Tanaka, *Bull. Chem. Soc. Jpn.*, **51**, 1655 (1978).

6) T. Kato, T. Nakanishi, and T. Fujiyama, *Bull. Chem. Soc. Jpn.*, **53**, 2173 (1980).

7) T. Kato, N. Ito, and T. Fujiyama, *Bull. Chem. Soc. Jpn.*, **53**, 2167 (1980).

8) D. V. S. Jain, *Indian J. Chem.*, **8**, 815 (1970).

9) D. V. S. Jain, *Indian J. Chem.*, **9**, 465 (1971).

10) Y. Murata and K. Nishikawa, *Bull. Chem. Soc. Jpn.*, **51**, 411 (1978).

11) K. Nishikawa and N. Kitagawa, *Bull. Chem. Soc. Jpn.*, **53**, 2804 (1980).

12) "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham (1962), Vol. III.

13) Y. Morino, Y. Nakamura, and T. Iijima, *J. Chem. Phys.*, **32**, 643 (1960).

14) D. T. Cromer, *J. Chem. Phys.*, **50**, 4857 (1969).

15) S. Miyake, "X-Sen No Kaisetsu," Asakura, Tokyo (1969).

16) A. Guinier and G. Fournet, "Small-Angle Scattering of X-Rays," John Wiley & Sons, London (1955).