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学 位 論 文 題 目　　Small-Angle X-Ray Scattering Studies on

　　　　　　　　　Inhomogeneity In Aqueous Mixtures

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Aqueous solutions of small organic molecules often show anomalous behavior in various transport and thermal properties. The formation of some kind of molecular aggregates or microinhomogeneity has generally been invoked for explaining these peculiarities. However, details of the microinhomogeneity are not clear as yet.

The small angle X–ray scattering (SAXS) method is one of the most direct ones to study microinhomogeneity. In the analysis, SAXS intensity curve ($I(s)$) is expanded as follows:

$$I(s) = r_0 - r_2 s^2 + r_4 s^4 - r_6 s^6 + \cdots \qquad \cdots (1)$$

where

$$r_{2i} = (1/(2i+1)i) <\Delta\rho_e(0)\Delta\rho_e(r)> r^{2i} 4\pi r^2 dr. \qquad \cdots (2)$$

Here s is the scattering parameter ($s = 4\pi\sin\theta/\lambda$, where 2θ is the scattering angle and λ is the wavelength of X–rays), $\Delta\rho_e(r)$ is the difference in the electron density from the average at position r, and $< \quad >$ denotes the ensemble average. The 'moment' determined through a SAXS measurement (r_{2i}) reflects various properties of the solution. The zero–angle scattering intensity ($I(0)$), which relates to the square of the number of molecules concerning the microinhomogeneity, is equal to r_0. The mean square fluctuation is concentration ($<N>(\Delta C_1)^2>$) is derived from $I(0)$. The correlation length (ξ), which indicates the average size of the microinhomogeneity, is calculated as $(r_2/r_0)^{0.5}$. These two (r_0 and r_2) have been chief concern in the previous SAXS studies.

Higher order coefficients in eq. (1), which have not been employed in previous SAXS studies, have a possibility to give additional information about microinhomogeneity as long as accurate enough SAXS data can be

accumulated. To understand the complicated mixing state of the molecular aqueous solutions, it is required to use as many kinds of indicators of microinhomogeneity as possible. Thus, in this thesis, the author has attempted to apply the higher order coefficients to studying the mixing state.

A point-focusing diffractometer with a double-bent LiF crystal monochromator as well as a position-sensitive proportional counter has been constructed to obtain accurate SAXS data. With this diffractometer, small-angle resolution of better than 0.42 is achieved. To evaluate the performance of the diffractometer, SAXS data on several pure liquids and aqueous solutions were measured. The results showed that this diffractometer produced incident beams intense enough to measure SAXS on solutions, making a collimation effect negligible simultaneously.

With the diffractometer mentioned above, it is possible to accurately determine the higher order coefficients. Accordingly, the following new parameter (χ) is proposed:

$$\chi = r_0 \, r_4 / r_2^2 \qquad\qquad \cdots \ (3)$$

Being related with r_4, this dimensionless parameter reflects the shape of I(s). Several theoretical SAXS functions were examined in order to understand the physical meaning of χ further, and χ has been interpreted to represent the size dispersion of fluctuating clusters formed in solution: a large/small χ corresponds to a large/small size dispersion.

To examine whether or not an analysis in terms of χ is meaningful in understanding the mixing state, the SAXS curve shape of 2-butoxyethanol (BE) and 1-propanol (abbreviated to NPA) aqueous solution has been extensively studies. The behavior of χ for the two aqueous solutions shows marked contrast.

BE aqueous solution has a lower critical solution temperature near room temperature, and its correlation length (ξ) and concentration fluctuation ($<N><(\Delta C_1)^2>$) showed very large variations with temperature and

concentration. In accordance with $<N><(\Delta C_1)^2>$ and ξ, χ markedly changed with both concentration and temperature.

On the other hand, NPA mixes with water at any concentration and at any temperature. ξ changed gradually with concentration but showed almost no change with temperature. The χ of NPA aqueous solution changed smoothly with concentration but varied only slightly with temperature; modest/immodest local structure change with temperature and concentration of NPA/BE aqueous solution is reflected on χ. Thus, it has been experimentally proved that χ is very sensitive to the mixing state and is accordingly available as a useful parameter.

In terms of the obtained χ's, a new piece of information about clusters formed in the two aqueous solutions can be discussed. In BE aqueous solution, χ is the smallest and is about 0.8 near the critical composition (around BE 5 mole%) at all the temperature studied and near the miscibility curve in phase diagram. In NPA aqueous solution, χ takes a minimum value and is about 1.1 around NPA 15 mole% at all the temperature studied. Because χ is small, it is predicted that clusters having a fairly well-defined size are dominant in these regions. This interesting suggestion should be ascertained in future work.

A use of the diffractometer constructed in this work has also made it possible to obtain SAXS data within a short time. Hence, the growth of nickel and iron silicates in the mixed solution of metal ethylene glycolates, water, and tetraethoxysilane has been monitored with SAXS. At an early stage of polymerization, the fractal dimension (D) increases, reaching a constant value while the reaction is still in progress. The D value suggests that the structure of the gels containing metals is different from that made without metals. Useful catalysts are prepared by the calcination of the gels. A relationship between the structures of the gel and of the catalyst is discussed.

論 文 の 審 査 結 果 の 要 旨

　出願者は博士後期課程において、点収束X線小角散乱測定装置を制作し、そ
れを用いて2－ブトキシエタノール水溶液と1－プロパノール水溶液各々の混
合状態を調べると共に、その装置の高速測定機能をシャープに生かした研究例
として、溶液中の金属クラスターの成長過程を追跡する研究をした。

　従来のX線小角散乱装置は、線収束であるために散乱角に広がりがあって精
度に問題があった。出願者は縦、横二方向に湾曲した結晶を用いて、入射X線
を点収束させ、そこから散乱されるX線を一次元検出器で検出する装置を設計
し製作した。その装置は従来のものに比べてX線をより有効に使うため、測定
時間が短縮されるうえに、散乱角の小さいところの散乱曲線の精度が高くなっ
た。その結果、散乱曲線から決められるパラメータが1つ増えた。その新しい
パラメータ、χがクラスターの大きさの分布を反映することを2－ブトキシエ
タノール水溶液とn－プロパノール水溶液の測定データで示した。2－ブトキ
シエタノール水溶液は、ある濃度、温度範囲で相分離をするが、n－プロパノ
ール水溶液は全濃度で均一混合液となる。前者は高温でχが小さくなり、ある
決まった大きさのクラスターができ、それが成長して最後に相分離すること、
後者では高温ほどχが小さくなる濃度域、変わらない濃度域、大きくなる濃度
域があることを初めて見つけ、有機化合物水溶液の混合状態の研究に新しい情
報を提供する実験法を確立した。

　また1回の測定が2時間以内で終わるという性能を有効に生かす試みとして、
水溶液中で金属シリケートクラスターの成長する過程をX線小角散乱法で調べ
た。その散乱曲線はクラスターの慣性半径とポロド勾配を与え、後者はフラク
タル次元に対応するので、成長過程におけるクラスターの形状変化に関する情
報を与えることを実際の系で示した。