

It should also be noted that in the crystal structure there was only one water molecule coordinated to each copper atom, *i.e.* one H<sub>2</sub>O/CuL.

This investigation demonstrates that small-angle X-ray scattering can be used as a complementary method to study the complex formation that leads to relatively large particles. The advantages with this method compared to the e.m.f. methods are that only small amounts of material are needed, and that the measurements can be made at a low ionic strength, or in a medium where e.m.f. methods are not applicable.

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## Solvent Environment and Mutual Interaction of Simple Solute Molecules in Solution as Revealed by Scattering Experiments. Examples: Hexamethylenetetramine in Water and DNA in Aqueous 1-1-Electrolyte Solution

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Hexamethylenetetramine (HMTA) in water and DNA in 1-1-electrolyte solutions are taken as model systems to obtain quantitative information about the perturbation of water in the vicinity of an uncharged solute molecule and to confirm quantitative information about the distribution of ions around a polyelectrolyte. They are taken as examples for the interaction of uncharged molecules in solution and for the interaction of polyelectrolytes in solution. They are taken because HMTA can be approximated by a spherical and DNA by a cylindrical distribution of scattering density. In these cases transformations from reciprocal to real space and *vice versa* can be performed by simple one-dimensional Fourier or Hankel transforms unaffected by averaging over all orientations. Fourier transformation of the scattering amplitude of the dissolved HMTA molecule shows the electron distribution within the solute molecule in agreement with its crystal structure and resolves some inhomogeneities of the solvent density around the solute molecule. The 'border area' of solute and solvent is especially well resolved and almost unaffected by termination errors and deviation from spherical symmetry. The obtained

solvent distribution is compared to the water structure in the clathrate HMTA hexahydrate and to simple models of HMTA in an ice-like water framework. The particle distribution functions of HMTA in water at several concentrations behave almost like those of a gas of hard spheres of 6 Å diameter, which is the nearest-neighbour distance of HMTA in the crystal. Thus solvent molecules around the dissolved molecules seem not to hinder the closest contact of the latter. Ion distributions around DNA when dissolved in a 1-1-electrolyte solution are calculated solving the Poisson-Boltzmann equation in cylindrical coordinates with appropriate parameters. Scattering curves of DNA in different simple salt solutions are calculated. Agreement with experiment confirms the calculations. In the cylindrical distribution functions of DNA in solution repulsive forces between the rods are reflected. In 0.2 M NaCl these forces keep the molecules away from each other by an average distance of almost twice their diameter. From the so-obtained excluded area the second virial coefficient of short rod-like DNA molecules is calculated and compared to results from light scattering. They agree within experimental error.

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### Investigations at the Tail End of the Small-Angle X-ray Region

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There is a region in the X-ray diffraction pattern between  $s=0.1$  and  $s=1.0$  ( $s=4\pi \sin \theta/\lambda$ ) which is not generally amenable to investigation by conventional small-angle X-ray techniques because the small-angle scattering is too faint. In addition, the large-angle pattern resulting from the close-order interatomic structure becomes significant in this region, and manifests itself relative to the small-angle part as an intense background. This is unfortunate because many problems in biology and the liquid state involve the determination of correlation lengths in the range 10–100 Å and it is precisely in this region of  $s$  that we would expect the diffraction phenomena resulting from these correlations to occur. A technique is described which uses high-scattering atoms to label certain preferred correlation distances in the system so that they can be isolated from the rest of the scattering. In this way it has been found possible to resolve the background scattering into its separate components. From this the large-angle contribution can be accurately evaluated, and by difference the small-angle portion is determined. The application of this technique to aggregation of long-chain alkanes is discussed.

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### Heterogeneities in Glasses and Small-Angle Scattering Methods

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The systematic study of heterogeneities in glasses is important both from the theoretical side (fluctuations in supercooled liquids) and for practical applications: fibre optics for optical communications systems and kinetics of phase separation and crystallization for synthesis of glass ceramics. Texture brought about by phase separation in glasses is in the range of 100–10000 Å which makes it particularly well suited for small-angle scattering studies. A review is presented of results obtained in this way for glassy systems according to their position in the immiscibility field: evaluation of (a) discrete precipitates in the case of a minor phase precipitation and (b) dense interconnected structures such as can be generated by a spinodal mechanism. Comparison is made with the results obtained by electron microscopy and first results obtained by small-angle scattering of neutrons.

#### I. Introduction

Glasses may be thought of as supercooled liquids which have attained progressively the characteristics

of a solid without crystallizing – as such they should reveal structural features analogous to those of liquids without the short-time mobility. The first small-angle X-ray scattering studies of glasses were made in an