

Interpretation of XRay Scattering from Solutions of LongChain Electrolytes on the Basis of a Spherical Micelle

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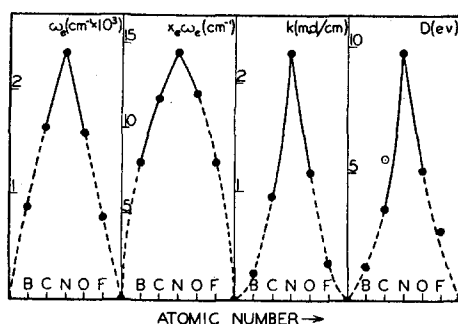
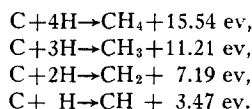
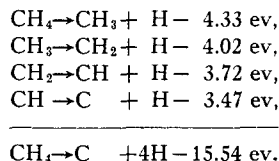


FIG. 2. Molecular constants of diatomic molecules
Be₂, B₂, C₂, N₂, O₂, F₂, Ne₂.

in CH₂) = 3.593 ev. Hence the Q_a values of this series are:



And the removal energies of the consecutive hydrogen atoms of methane are:



It is believed that these simple considerations lend weight to the lower value of the heat of dissociation $L(\text{C}) = 5.888 \text{ ev.}$

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Interpretation of X-Ray Scattering from Solutions of Long-Chain Electrolytes on the Basis of a Spherical Micelle

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June 28, 1948

X-RAY diffraction measurements on isotropic aqueous solutions of long-chain electrolytes have been interpreted largely on the basis of a lamellar micelle;¹ thus "spacings" calculated by the Bragg equation have been assigned to various identity periods in this structure. Hartley,² however, has long maintained that the micelle

must exist in spherical form. Recently a cylindrical model has been discussed by Harkins;³ this latter is, however, characterized by Bragg law "spacings." It is indicated below (1) that the observed x-ray diffraction patterns can arise from a system of spherical micelles and (2) that Bragg law "spacings" may be meaningless.

Unfortunately no diffraction measurements have as yet been reported in which the absolute intensity of the scattered radiation is known as a function of the scattering angle. The position of the rather broad diffraction peaks has been studied as a function of electrolyte concentration; some qualitative observations have been made on the variation of relative intensities of these peaks, or bands, with concentration.⁴

The highly simplified model considered here is one of spherical micelles of uniform radius, a_0 , whose short range order is characterized by a radial distribution function, $G(r)$. Ordinarily such distribution functions in liquid systems are calculated by means of the Fourier transform from diffraction data in which the absolute intensities of the scattered radiation are known as a function of the scattering angle.⁵ Since in the present case no such data are available the reverse process will be employed; namely, the angular variation in intensity of the scattered radiation will be calculated on the basis of an assumed radial dis-

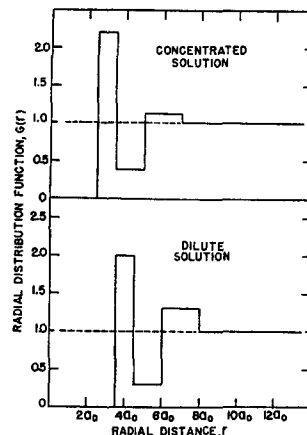


FIG. 1. Radial distribution functions for spherical micelles in concentrated and dilute solutions employed for the calculation of x-ray scattering. The radius of the micelle, a_0 , is taken as 16 Å.

tribution function. All that can be expected from this treatment is qualitative agreement with respect to the form of the calculated and observed scattering curves. Under these conditions an extremely simple and highly approximate form of distribution function may be used.

Diffraction from two solutions of long-chain electrolyte, one dilute and the other concentrated, will be considered. The appropriate radial distribution functions employed are shown in Fig. 1 while the scattering curves calculated therefrom⁶ are plotted in Fig. 2. These calculations are based upon a micelle 16 Å in radius and for Cu K α radiation. The circles indicate those points for which the calculations were made.

These calculated scattering curves agree in form with those reported by Mattoon, Stearns and Harkins, while the relative intensities display the observed variation with concentration of long-chain salt. In a similar fashion the diffraction band observed at larger angles may be attributed to the short range ordering of hydrocarbon chains in the interior of the spherical micelle. On the basis of the model here considered, "spacings" calculated by the application of the Bragg equation to the position of the diffraction peaks are meaningless.⁷

It is thus shown that a lamellar model is not required to explain the x-ray diffraction patterns obtained from solutions of long-chain electrolytes. On a qualitative basis these patterns may be satisfactorily interpreted by recourse to a model of spherical micelles characterized with respect to relative position by a radial distribution function. This, of course, does not prove the validity of the spherical model. What it does indicate, in the light of our present experimental knowledge, is that x-ray measurements alone do not allow a decision between the lamellar and spherical models for micelles. Since a periodic structure cannot be demonstrated unambiguously, the "spacings" calculated

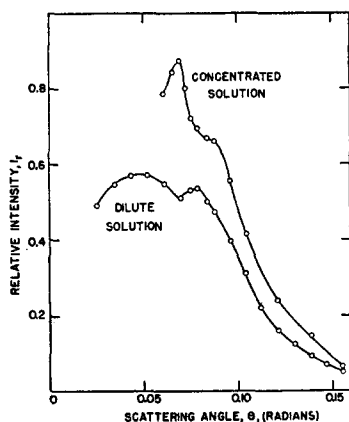


FIG. 2. The calculated scattered x-ray intensity curves for concentrated and dilute solutions of spherical micelles. Circles indicate those values which were calculated.

by the application of the Bragg equation to the diffraction patterns must be considered as of little significance.

The author would like to acknowledge helpful discussion and criticism by Dr. Bruno H. Zimm.

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Continuous Spectra and OH Absorption in Carbon Monoxide—Oxygen Explosions*

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June 11, 1948

THE use of a steel spherical bomb is not new to investigators in the field of combustion, but, in general, its use has been restricted for the purpose of obtaining pressure measurements, flame speeds, and experiments involving over-all radiation. The spectrum of an explosion of CO and oxygen of stoichiometric mixture is similar to a CO and oxygen flame in that the banded structure is superposed on a strong continuous background which extends throughout the visible into the ultraviolet. The intensity of this continuum frequently prevents sufficient contrast to allow resolution of the structural part of the spectrum; this single factor may account for the paucity of spectroscopic studies of combustion processes.

The brilliant flash which accompanies the explosion of CO and oxygen in a spherical bomb suggested the possibility of spectroscopic studies with an instrument of good dispersion without a prohibitive number of explosions. The steel bomb referred to in this discussion has a volume of 7 liters, and is equipped with two 1-in quartz windows diametrically centered. The mixture is ignited at the center of the sphere by a pair of tungsten electrodes connected to a common spark coil. The data are from spectrograms obtained with a Baird 2-meter grating spectrograph with 4A/mm dispersion. Figure 1 contains two curves founded on a series of single explosions in a bomb with a mixture of CO and oxygen in varying proportions. The carbon monoxide was commercially prepared and has 1.5 percent of nitrogen and hydrogen as impurities. Curve A shows the effect of increased oxygen on the intensity of the continuum. When the explosive mixture contained

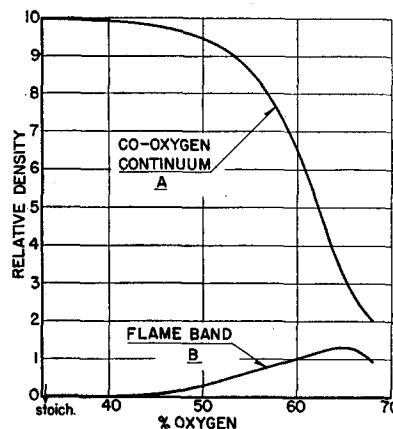


FIG. 1. Curve A: Density of the continuum at 3400A as a function of percent oxygen divided by the density at stoichiometric mixture. Curve B: The average density of several lines of a CO flame band of similar intensity ($\sim 3400\text{\AA}$) above the density of the adjacent continuum. Thus, at 65 percent oxygen the density of a line would lie at about 1.3 above Curve A. The data for these curves are based on single explosions through a 2-meter grating spectrograph in the second order with a 25-micron slit on Eastman II-O plates.