

An Objective Method for Studying Electron Diffraction by Gases

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TABLE I. Micelle thickness changes due to "oils" dissolved in aqueous solutions of pure potassium myristate (KC_{14}) and pure sodium lauryl sulfate ($\text{NaC}_{12}\text{SO}_4$) at 25°C.

"Oil"	Percent by wt. of soap		Grams "oil" per 100-g soap solution	Simple Bragg spacing $d_M \pm 1\text{\AA}$	M-Spacing changes due to "oil" $\Delta d_M \pm 2\text{\AA}$
A. benzene	7.16	KC_{14}	2.66 ^b	52.0	+11.7
ethyl benzene	8.65	$\text{NaC}_{12}\text{SO}_4$	2.81 ^c	44.0	+ 6.7
<i>n</i> -heptane	8.65	$\text{NaC}_{12}\text{SO}_4$	1.46 ^d	44.4	+ 7.1
B. <i>n</i> -heptanol	7.16	KC_{14}	2.4 ^b	42.0	+ 1.7
<i>n</i> -heptanol	9.82	KC_{14}	3.0 ^d	41.0	+ 0.7
<i>n</i> -heptanol	8.65	$\text{NaC}_{12}\text{SO}_4$	2.98 ^d	39.0	+ 1.7
<i>n</i> -octanol	8.65	$\text{NaC}_{12}\text{SO}_4$	2.21 ^d	39.6	+ 2.3
<i>n</i> -decanol	8.65	$\text{NaC}_{12}\text{SO}_4$	2.16 ^d	37.5	+ 0.2
<i>n</i> -decanol	7.16	KC_{14}	1.83 ^b	42.5	+ 2.2
<i>n</i> -decylamine	8.65	$\text{NaC}_{12}\text{SO}_4$	1.74 ^d	36.0	- 1.3
<i>n</i> -decylamine	8.65	$\text{NaC}_{12}\text{SO}_4$	1.85 ^c	35.3	- 2.0

* Without "oil," at any concentration d_M for $\text{NaC}_{12}\text{SO}_4$ is 37.3 and for KC_{14} is 40.3A.

^b Just saturated.

^c The saturation value is slightly less than this figure.

^d Slightly under-saturated.

total energy of adhesion is 93. For *n*-heptanol these values increase to 92 and 165, respectively. The attraction of water is not sufficient to allow solubilized hydrocarbon molecules to pass from the interior of a micelle into its soap layer and contact the surrounding water. However, the larger attraction of water for the hydroxyl groups of alcohols might enable these molecules to penetrate and become part of the layer of oriented soap molecules.

If a cetyl alcohol monolayer is spread on water and the area adjusted to 25\AA^2 per molecule, the film pressure at 20°C is only 1.2 dynes/cm. If the aqueous subphase is made $3(10)^{-6}$ molar sodium cetyl sulfate, and the total film area kept constant, detergent molecules penetrate into the alcohol monolayer until at equilibrium the film pressure increases² to 50 dynes/cm—an increase of over 40 times. To squeeze detergent molecules out of this layer would require a lateral film pressure equivalent to 200 atmospheres, and the alcohol monolayer would remain under this pressure.

Considering these relations, it is to be expected that molecules of long-chain alcohols, amines, or similar polar-nonpolar compounds, when dissolved in an aqueous solution of soap or similar colloidal electrolyte, will actually *penetrate* between the soap molecules and produce a larger mixed micelle. Presumably, the polar groups are between the ionic groups of micellar soap molecules, both being in contact with the water. This should reduce the repulsion between the ionic groups and thus make the micelle more stable and larger. These expectations seem to be substantiated by the following experimental results.

The micelle thickness is not appreciably altered, within the experimental error, by dissolved *n*-alcohols and *n*-decylamine (Table IB).

By a method of uncertain accuracy developed by Mattoon, the average numbers of soap and "oil" molecules per micelle, n_s and n_o , are calculated from the modified long-spacing x-ray *I*-band, assuming that it measures the average distance between the nearest micelles. For a 15 percent aqueous solution of potassium laurate, this calculation gives $n_s \approx 76$; when saturated with ethyl benzene,

$n_s \approx 150$ and $n_o \approx 70$; when saturated with *n*-dodecanol, $n_s \approx 180$ and $n_o \approx 68$. Although these numbers may not be exact, they indicate larger micelles with either hydrocarbons or alcohols dissolved.

Solubilized hydrocarbons change the critical micelle concentration by a small amount. However, 3 percent of *n*-butanol decreases³ the *c.m.c.* of dodecyl ammonium chloride by 67 percent and as little as 0.1 percent of *n*-heptanol decreases the *c.m.c.* of potassium myristate by 33 percent.

H. Oppenheimer here has found that *n*-heptanol is more than twice as soluble as *n*-heptane in aqueous potassium myristate solutions. Also, if *s* represents the "oil" solubility and *c* the soap concentration, then $(\partial s / \partial c)_T$ increases with increasing *c* for hydrocarbons and apparently decreases slightly for *n*-heptanol.

The contrast in the behavior of hydrocarbons and of long-chain alcohols and amines, cited above, indicates that hydrocarbons *solubilize* in the interior of the micelle, whereas alcohols and amines *penetrate* into the monolayer of soap molecules making up the double-layer micelle.

The total solubility of "oils" in aqueous micellar solutions may be classified as follows:

1. Solubility in water, or in non-micellar solution.
2. Solubility by adsorption on the outer surface of the micelle.
3. *Solubilization* in the middle of the micelle.
4. Solubility by *penetration* into the micellar soap layer.

* This investigation was carried out under the sponsorship of the Reconstruction Finance Corporation, Office of Rubber Reserve, in connection with the Government's synthetic rubber program.

¹ R. W. Mattoon, R. S. Stearns, and W. D. Harkins, *J. Chem. Phys.* **15**, 209 (1947).

² W. D. Harkins, L. E. Copeland, and B. Gordon, "Surface chemistry," *Pub. 21*, Am. Assoc. for the Advancement of Science, p. 79, 1943.

³ M. L. Corrin and William D. Harkins, *J. Chem. Phys.* **14**, 640 (1946).

An Objective Method for Studying Electron Diffraction by Gases

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August 21, 1947

THE device described in the previous letter produces a microphotometer trace which may be used for objective study of electron-diffraction negatives. Hitherto these have been interpreted mainly by visual observation. The microphotometer trace as obtained from a standard diffraction negative is limited in usefulness since the molecular portion of the scattered intensity is superimposed on a steeply falling background. The suggestion has been made^{1,2} to insert a rotating sector into the diffraction camera which can flatten the background and accentuate the oscillating portion of the diffraction pattern. In practice, this method is rather inconvenient to apply.³ We have

found it possible to perform the necessary mathematical manipulation directly on the intensities obtained from the linear-response region on the improved microphotometer trace. The procedure could perhaps be further improved by employing in combination with the improved tracing method a simplified sector technique³ which partially reduces the background effect. The advantage of the simple sector is to extend the range of scattering angle included in the linear-response region of the photographic plate.

The intensity of electron scattering by gases is proportional to

$$\sum_i^N (S_i/s^4) + \sum_i^N (f_i^2/s^4) + \sum_{ij}^N (f_i f_j/s^4) A(r_{ij}, s), \quad (i \neq j). \quad (1)$$

The symbols are explained in a review article by Brockway.⁴ A simple sector would multiply this intensity by some convenient power of s . The incoherent term S_i can usually be neglected and the scattering factors of the atoms in the molecule may generally be written as $f_i = f \times Z_i$, where f is a general shape function. In our method the intensities for closely spaced s values are derived from the microphotometer trace and are multiplied by $1/f^2$ and by the required power of s to remove the s^4 from the denominator of (1). Effectively, this process gives

$$\sum_i^N Z_i^2 + \sum_{ij}^N Z_i Z_j A(r_{ij}, s), \quad (i \neq j), \quad (2)$$

which is the molecular scattering function superimposed on a level background. The curve obtained in this way may be treated by the correlation procedure as well as the radial-distribution method. Although the factor s^n/f^2 usually applies, it is occasionally necessary to make a correction for the possible variation in the shapes of the scattering factors for small s values and when atoms of very different atomic numbers are present in the molecule.

¹ C. Finbak, Avh. Norsk Vidensk.-Acad., Oslo, M.-N.KI., No. 13 (1937).

² P. P. Debye, Physik. Zeits. 40, 66, 404 (1939).

³ C. Finbak, O. Hassel, and B. Ottar, Arch. f. Math. og Nat., Oslo B44, No. 13 (1941).

⁴ L. O. Brockway, Rev. Mod. Phys. 8, 231 (1936).

An Improved Microphotometer Trace of Radially Symmetric Patterns

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August 21, 1947

A DEVICE has been constructed for producing a smooth and accurate microphotometer trace from radially symmetric patterns by minimizing the variations due to the granular character of the emulsion. This device spins the negative while it is being traced. A previous suggestion to this effect has been made by Degard, Pierard, and van der Grinten.¹ The improved trace obtained in this manner makes it possible to use an objective method for

analyzing electron-diffraction patterns of gases which consist of oscillations about a steeply falling background.

The spinning attachment shown in Fig. 1 is attached to

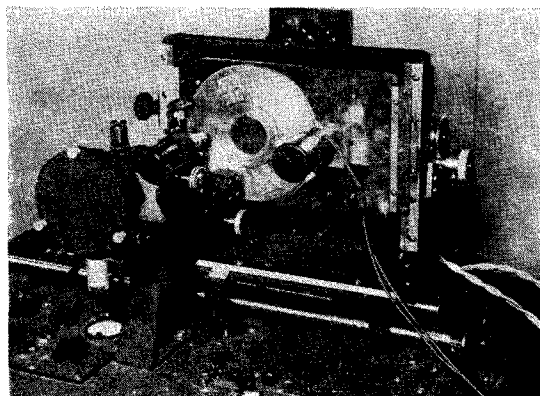


FIG. 1. Photograph of the rotating attachment in place on the Leeds and Northrup microphotometer.

the Leeds and Northrup microphotometer and consists of a geared ring large enough to hold a plate 2 in. by 4 in. The geared ring is mounted into its frame on adjustable ball bearings and is spun by a 0.01-hp alternating current motor whose maximum rated speed is 7000 r.p.m. The gear ratio is 12.5:1, and in practice the motor speed is controlled by an auto-transformer since its maximum speed is not required. The photographic plate is centered by means of cross-hairs on a Lucite disk which is removed for the tracing. The plate is then aligned with respect to the optical system on the microphotometer and is ready to be spun and traced. The improvement of the trace by averaging over the grains of the emulsion is shown in Fig. 2, where A is the

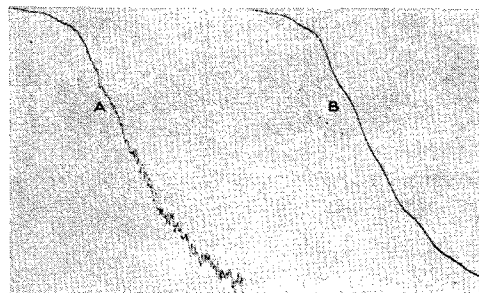


FIG. 2. Microphotometer traces of an electron-diffraction pattern: A , without rotation of the plate, B , with rotation using the same slit system.

trace of the stationary plate and B is the trace of the rotated plate. The microphotometer beam was focused to about 0.02 mm by 0.2 mm on the Eastman commercial plate and was the same for both traces.

¹ C. Degard, J. Pierard, and W. van der Grinten, Nature 136, 143 (1935).