same solvent. The pure diphenylbenzidine separates on cooling; after filtering off and washing with alcohol until the washings fail to yield a white cloud upon dilution with water, the product is dried at 110°. The yield is 60–65%,[2] m. p. 244–245° (uncorr.).

About 10% of the crude product is insoluble in boiling xylene, and 25–30% remains in solution in the cold mother liquor. This more soluble product probably consists largely of 2,2'-dianilinodiphenyl. One liter of xylene dissolves 0.3 g. of diphenylbenzidine at 25°.

The indicator may be employed satisfactorily by mixing 1 drop of a 0.1% solution in sulfuric acid with 10 cc. of a mixture of equal parts of glacial acetic acid and sirupy phosphoric acid. By the use of such a solution, good end-points are obtained with 0.01 N standard solutions, provided stirring has been continuous and thorough.

(2) This method has been repeated by Dr. R. E. Montonna and Mr. L. T. Jilk, of this Laboratory, who have obtained a yield of 50% when working on a ten times larger scale.

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Heat of Vaporization of a Pure Substance from the Measurement of the Temperature at Two Points and the Vertical Distance between Them

BY S. C. COLLINS

Consider a vertical tube containing a small quantity of the pure liquid and its saturated vapor. Sufficient heat is applied to the liquid to maintain the desired temperature. Since the insulation is not perfect, the walls of the tube are kept moist by condensation of the vapor. The temperature at A, a point near the lower end, will be slightly higher than that at B, a point near the upper end, because the pressure is higher. Let the difference in temperature, dT, be measured with a differential thermocouple. Denoting the difference of pressure by dp, $dp = gh/V'$, where V' is the specific volume of the saturated vapor, g the acceleration of gravity and h the vertical distance between the points A and B.

Substituting for dp in Clapeyron's equation

$$L = \frac{dp}{dT} T(V' - V) \qquad (1)$$

its value, gh/V', one obtains the relation

$$L = \frac{T}{dT} gh \left(1 - \frac{V}{V'} \right) \qquad (2)$$

At temperatures not too near the critical point V' may now be calculated with sufficient precision by means of the equation of state for ideal gases. The value of V, the specific volume of the liquid need be known only roughly.

In the case of water vapor at 100° the calculated value of V' is incorrect to the extent of 1.6%. The error in the latent heat, L, resulting from the use of the calculated value of V' in equation (1) is 1.6%, whereas the same value used in equation (2) produces an error of only 0.001%.

To illustrate the order of magnitude of the quantities to be measured the following table is prepared. The length of the tube is assumed to be 20 meters. The values of dT were calculated from existing data.

Substance	Temp., °C.	dT
H_2O	50	0.0265
	100	.0324
CCl_4	50	.304
	65	.343

It is anticipated that difficulties in preparing samples of sufficient purity and in measuring dT with the required precision may prove serious but not insurmountable.

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x-Ray Diffraction Studies of Built-up Films of Long-Chain Compounds

BY G. L. CLARK, R. R. STERRETT AND P. W. LEPPLA

The technique developed by Blodgett and Langmuir[1] for transferring monomolecular films of long-chain compounds from a water surface to a glass surface and the opportunity thus afforded to apply a known number of layers of molecules, one on top of the other, has proved to be exceedingly valuable in x-ray diffraction studies of long-chain compounds. For a number of years studies have been made on films of these compounds produced by melting the substances into a thin film on a suitable backing or by evaporating a solution of the substance in a suitable solvent. The unknown factor has been the actual number of molecular layers in the oriented film. With a little practice, we have now found it possible to build up successive monomolecular films of vari-

(1) THIS JOURNAL, 56, 495 (1934); J. Franklin Inst., 218, 143 (1934).

ous substances, not only on glass but on several plane and curved metal surfaces. With the latter type of backing, of course, the necessity for oscillation of the specimen during the x-ray exposure is removed.

We have now made diffraction patterns for stearic acid from one up to 187 layers, and for several other acids and derivatives. Blodgett and Langmuir found that a trace of calcium ion in the water upon which the monomolecular films were produced, was very highly advantageous in the successful transference of the film from the water to glass. A calcium-ion concentration corresponding to a saturated solution of calcium carbonate is, indeed, very helpful in this process.

The question then arises as to whether the film is actually stearic acid or calcium stearate. From very careful measurements the long spacing for these built-up layers transferred from water containing calcium ion is found to be 47.55 Å., which evidently corresponds to the thickness of two monomolecular films turned in opposite directions (the methyl group end of the molecule turns in when the plate is pushed into the film trough, and the carboxyl end oriented down in the water, turns in, when the plate is pulled out). The long spacing for a film of pure synthesized calcium stearate studied by the older methods is found to be 47.53 Å., for the length of two molecules. It is clear, therefore, that soap formation has actually taken place on the water surface. In order to test this conclusion further it was possible, after numerous trials and by forming new films for each step, to take up stearic acid films from the surface of purest distilled water. The spacing for this specimen is 46.05 Å., which is still appreciably greater than the value for a film from molten stearic acid, namely, 39.62 Å. Palmitic acid on water containing calcium ion gives the principal spacing of 43.50 Å., again corresponding to the soap, and myristic acid a spacing of 39.55 Å.

Aside from the fact that this method permits the study of reactions of this type and also makes possible the preparation of films in the ideal condition since each layer is distinctly monomolecular, it follows that very interesting data with respect to intensities of diffraction interferences in various orders can be obtained. A few of these are presented here as typical examples. The values are given relative to a standard intensity of 10 for the first order of the long spacing for 61 layers of stearic acid (or actually calcium stearate)

on polished cadmium. The temperature in all cases was 25° and the pH of the solution containing Ca^{++} was 8.7.

INTENSITY DATA

Stearic acid (on water containing Ca^{++}) transferred to cadmium

| Layers | Intensity of orders of diffraction for long spacing | | | | |
	1	2	3	4	5
45	7	2	3.5	0	1
61	10	2	4.5	0	0
85	12	3	5.9	0	2.5
121	15	3	7.1	0.5	2.0
187	20	5	10	1.5	3.1

Palmitic acid (on water containing Ca^{++}) transferred to brass

55	Incom-	1.2	4	0	1.1
85	pletely re-	3.5	8	0.5	3
	solved				
151	23	4.5	10	.5	4

Stearic acid on pure water transferred to brass

71	7	0.5	2.5	0	0
125	12	3	4.7	0	1

The sharpness of the interferences depends upon the number of layers in the film. For 25 layers of calcium stearate, the first order interference is so sharp that it appears as a spot, while for increasing number of layers the spot lengthens gradually into an arc indicative of less perfect orientation. Faint but perfectly definite patterns are obtained with 9 layers. Further work with prolonged time is under way to ascertain the minimum number of layers required to produce any diffraction effects.

It is quite clear from these preliminary investigations that this new technique will be of very great value both in studies of the theory of diffraction from these films of long chain compounds and for practical applications of diffraction information to the lengths, structures and properties, such as lubrication, residing in these long molecules. However, there is an even wider scope of possibilities as illustrated by the following experiment. A solution of ferric chloride in petroleum ether is spread on water containing ammonium hydroxide. A film of ferric hydroxide is formed which can be transferred as easily to glass as stearic acid. The film can be formed upside down by floating a benzene solution of ammonia on an aqueous solution of ferric chloride.

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