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RECEIVED MARCH 29, 1938

COMMUNICATIONS TO THE EDITOR

COMPARISON OF X-RAY PHOTOGRAPHS TAKEN WITH X AND Y BUILT-UP FILMS

Sir:

Some time ago Mr. Clifford Holley and I reported [*Phys. Rev.*, **52,** 525 (1937)] that X films of calcium stearate have approximately the same grating-space as Y films of barium–copper stearate. In Figs. 1 and 2 are shown some of the photographs taken with films built by Dr. Katharine Blodgett on the basis of which this statement was made. They show Lα and Lβ lines of tungsten in the first three observable orders on both sides of the direct beam. Figure 1 was taken with an 1100 layer Y film of barium–copper stearate, Fig. 2 with a 300 layer X film of calcium stearate. In both cases the direction of dipping was parallel to the axis of rotation of the film. It can be seen that the photograph taken with the X film is essentially the same as the one taken with the Y film with respect to both the grating-space and the relative intensities of the various orders. The grating-spaces of these films, corrected for refraction and based upon the ruled grating wave length scale, are: Y film of barium–copper stearate, 50.47 Å.; X film of calcium stearate, 50.12 Å.

Porter and Wyman have shown [THIS JOURNAL, **59,** 2746 (1937)] that the contact potentials of X films increase with the number of layers, whereas those for Y films remain constant. The X-ray photographs, however, seem to be independent of the contact potential. The potentials of an X and a Y film of calcium stearate were measured, after which photographs of the kind shown here were taken. The photographs were much the same as those shown, despite the difference in the contact potentials of the films before exposure. The apparent grating-spaces of the two films in the first order differed by about 1%, the X film having the greater spacing. The two films were built from 10^{-4} molar solutions of calcium chloride. Castor oil was used as piston oil for the X film, and oleic acid for the Y film.

Fig. 1.—Three orders of tungsten L-spectra from Y film.

Fig. 2.—Three orders of tungsten L-spectra from X film.

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SEYMOUR BERNSTEIN

RECEIVED APRIL 22, 1938

PRESSURE–AREA RELATIONS OF MONOLAYERS AT THE SOLID–LIQUID INTERFACE

Sir:

While the pressure $F = \gamma - \gamma'$ of a monolayer on water may be determined by a film balance, no method has been known for obtaining F at a solid–liquid interface. In order to determine this value the contact angle θ_1 between the plane surface of the solid and the pure liquid is found by an improved form of the tilting plate method, so arranged that the surface of the liquid can be kept clean by sweeping. Then the pure liquid of surface tension γ_l, *e. g.*, water, is replaced by a solution of the desired solute, of tension $\gamma_{l'}$ and the new contact angle θ_2 is determined. Then

$$\gamma_s = \gamma_{sl} - \gamma_l \cos \theta_1 \qquad (1)$$

$$\gamma_s' = \gamma_{sl'} - \gamma_{l'} \cos \theta_2 \qquad (2)$$

where *s* indicates a solid.

Tests seem to indicate that the contamination of the interface solid–vapor with the solute can often be made so small that $\gamma_s = \gamma_{s'}$ so in this case (1) $-$ (2) gives $\gamma_{sl} - \gamma_{sl'} = F = \gamma_l \cos \theta_1 - \gamma_{l'} \cos \theta_2$ where the quantities in the right hand term can be measured. Now since

$$\left(\frac{\partial F}{\partial a}\right)_T = -\left(\frac{\partial \gamma'}{\partial a}\right)_T$$

where a is the activity of the solute, the adsorption may be obtained by the equation of Gibbs. This gives the area a per molecule adsorbed. The area A, which refers to the total number of molecules of solute in the monolayer, is slightly less than a, since some molecules are already present.

Of the measurements made thus far, only those in which butyl alcohol is a solute are cited here. The relations are given in Fig. 1 for films of this substance at (1) the water-vapor, (2) the water–solid paraffin, and (3) the water–stibnite interface.

For a film which acts as a perfect gas $FA/kT = 1$. Since at a film pressure of 40 dynes per cm. the pressure per sq. cm. is of the order of 700 atmospheres, high pressures are involved.

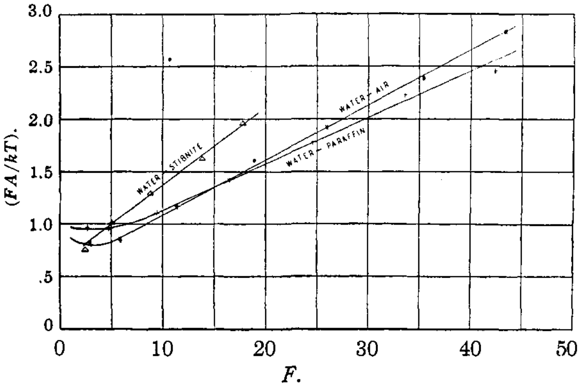

Fig. 1.—Pressure-area relations of films at the solid-liquid interface.

Obviously from Fig. 1 the films are gaseous at low pressures. If solid or liquid at high pressures there should be a vertical drop in the curve for the transition region, and then an ascending straight line which extrapolates through the origin. Thus, even though these monolayers are adsorbed on a solid they are nevertheless gaseous. Acetic acid films between water and solid paraffin are also gaseous.

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CHICAGO, ILL. FREDERICK M. FOWKES

RECEIVED APRIL 22, 1938

STEROLS. XXXIV. THE ISOLATION OF HEXAHYDRO-OESTRADIOLS FROM HUMAN NON-PREGNANCY URINE

Sir:

While no investigations of the steroid content of non-pregnant female urine have been reported, it is known that very little oestrogenic material is present [Loewe and Lange, *Klin. Wochschr.*, **5**, 1038 (1926)]. We have now isolated from this source, after removal of a small amount of pregnanediol, two isomeric diols, $C_{18}H_{30}O_2$, the more insoluble melting at 242° and giving a good depression in melting point with pregnanediol and *allo*-pregnanediol. *Anal.* Calcd. for $C_{18}H_{30}O_2$: C, 77.6; H, 10.9. Found: C, 77.4; H, 10.8. The diacetate melted at 160°. *Anal.* Calcd. for $C_{22}H_{34}O_4$: C, 72.9; H, 9.5. Found: C, 73.2; H, 9.7. The second isomer melted at 204°. *Anal.* Calcd. for $C_{18}H_{30}O_2$: C, 77.6; H, 10.9. Found: C, 77.6; H, 10.8. It gave a diacetate melting at 160°, which gave a good depression in melting point with the first diacetate. *Anal.* Calcd. for $C_{22}H_{34}O_4$: C, 72.9; H, 9.5. Found: C, 72.8; H, 9.5. These compounds are present in non-pregnancy human urine, but they do not appear present in pregnancy urine for their easy mode of isolation makes it extremely unlikely that they would have been overlooked in our extensive investigation of the steroid content of this material. Both diols are hexahydro-oestradiols, for they yield equilenin on heating with platinum black. Furthermore, the less abundant lower melting and more soluble isomer is identical with a diol obtained by the catalytic hydrogenation of oestrone according to the method of Dirscherl [*Z. physiol. Chem.*, **239**, 53 (1936)]. This latter diol yields a diketone m. p. 148° (*Anal.* Calcd. for $C_{18}H_{26}O_2$: C, 78.8; H, 9.5. Found: C, 79.0; H, 9.6), different from the diketone m. p. 124° (*Anal.* Calcd. for $C_{18}H_{26}O_2$: C, 78.8; H, 9.5. Found: C, 79.2; H, 9.8) obtained from the diol, m. p. 242°, so the two carbinols must be stereoisomers, differing at least in regard to the configuration at C-5 or C-10. Neither diol is precipitated by digitonin, and both are saturated to bromine.

Since these diols, which evidently arise from the biochemical reduction of oestrone, are not present in pregnancy urine, their presence in non-pregnancy urine indicates that they are not merely enzymatic reduction products, but are associated with the use of oestrone when it functions as a hormone, arising from the latter by reductive processes as do the various carbinols and ketones,