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## COMMUNICATIONS TO THE EDITOR

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### DIMENSIONS OF SOAP MOLECULES AS SUPPOSEDLY DEDUCED FROM SURFACE TENSION MEASUREMENTS

Sir:

The surface tension measurements of Du Noüy [*Phil. Mag.*, [6] **48**, 664 (1924)] as carried out with the ring method were recently reproduced by Washburn and Berry [THIS JOURNAL, **57**, 975 (1935)] using the capillary rise method for sodium palmitate solutions. The equilibrium surface tension-concentration curve shows three minima and the same number of maxima.

According to the Gibbs theorem for these concentrations no adsorption at all takes place. Instead, the interpretation of Du Noüy as now repeated by Washburn and Berry introduces the hypothesis that the minima are due to condensed films on the water surface, but differing in orientation corresponding to the three dimensions of the adsorbed molecule. No other confirmation for the validity of this view has been available.

However, the assumptions on which the theory of Du Noüy is based—besides contradicting the thermodynamics of Gibbs—are also objectionable. First, the acceptance of the supposition that the adsorbed quantities are proportional to the concentrations is quite untenable. Second, in calculating the surface tensions the possible influence of the angle of contact was completely disregarded, because it was tacitly taken for granted that perfect wetting always occurred.

This point, alone, seems to lead to a very plausible explanation of the experiments, if they are compared with the wonderful results of Miss Blodgett [THIS JOURNAL, **57**, 1007 (1935)], who proved the existence of polymolecular soap films of alternating orientation as adsorbed on glass and other solids, when in contact with the solutions. The same phenomenon, unfortunately, is to be expected at the platinum ring of Du Noüy as well as at the walls of the glass tubes.

As Miss Blodgett showed, the first layer of molecules is always fixed with the active groups toward the adsorbent, whereas the paraffin groups are directed toward the solution. Therefore, with increasing concentration the glass or platinum is covered at first with a film of paraffin

character which, as is well known, repels water. But the second layer may be orientated in the opposite direction, causing a decrease of the angle of contact. Consequently the apparent surface tension rises, unless a new paraffin surface is deposited.

The author in collaboration with E. J. Better applied the bubble pressure method, as being independent of the angle of contact, for the measurement of oleate solutions. Only one minimum was found, and that at a higher concentration than any of the minima of Du Noüy.

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### THE RELATIONSHIP OF ERGOTOCIN TO ERGOMETRINE

Sir:

Dudley and Moir [*Brit. Med. J.*, i, 520 (1935)] recently described the isolation from ergot of an alkaloid, chemically and pharmacologically different from any of the then known alkaloids of ergot, which they named ergometrine.

Although there were strong grounds for believing that ergotocin [Kharasch and Legault, THIS JOURNAL, **57**, 956 (1935)] was identical with ergometrine, Kharasch and Legault have not adopted this view, but have suggested that the two substances may be different [*e. g.*, *Lancet*, i, 1243 (1935)]. They have now published a formula,  $C_{21}H_{27}O_3N_3$ , for ergotocin [THIS JOURNAL, **57**, 1140 (1935)], while analyses of ergometrine and its salts now very accessible [Dudley, *Pharm. J.*, iv, **80**, 709 (1935)] indicate the formula  $C_{19}H_{23}O_2N_3$ , which is still being critically examined. [Further work on this substance since this "Communication" was dispatched (July 11, 1935) affords convincing evidence that this formula is correct.]

**Ergometrine:** *Anal.* Calcd. for  $C_{19}H_{23}O_2N_3$ : C, 70.15; H, 7.08; N, 12.92. Found: C, 70.0; H, 6.96; N, 12.91.

**Ergometrine Hydrobromide.** *Anal.* Calcd. for  $C_{19}H_{23}O_2N_3 \cdot HBr$ : C, 56.15; H, 5.91; N, 10.35; Br, 19.71. Found: C, 56.24; H, 6.19; N, 10.71; Br, 19.76.

**Ergometrine Hydrochloride.** *Anal.* Calcd. for  $C_{19}H_{23}O_2N_3 \cdot HCl$ : C, 63.08; H, 6.64; N, 11.62; Cl, 9.82. Found: C, 63.1; H, 6.81; N, 11.29; Cl, 9.54.

**Ergometrine Oxalate:** *Anal.* Calcd. for  $C_{19}H_{23}O_2N_3 \cdot$