

Surface potential of a two-dimensional film of pentadecanoic acid in the coexistence region*

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We report measurements of the change in the work function of a pH-2 water surface upon spreading a monolayer of pentadecanoic acid. The measurements were made as a function of density at a temperature of 20.1°C, which is below the critical temperature for this monolayer. Large variations in the work function were observed in the density range corresponding to the region in which the liquid and vapor phases of the monolayer coexist, offering further evidence for the presence of two distinct phases.

It is well known that the contact potential between an electrode and a water surface is a function of their surface conditions. The contact potential is altered by the presence of a monomolecular film on the water surface, and the change in contact potential upon spreading the monolayer is known as the surface potential.¹

Recent measurements by ourselves² and by Hawkins and Benedek³ have shown that monolayers of pentadecanoic acid [$\text{CH}_3(\text{CH}_2)_{13}\text{COOH}$] exhibit a gas-liquid coexistence curve, with the surface pressures of the coexisting phases being equal to within experimental accuracy, at any given temperature below the critical. In order to provide further evidence with regard to the question of whether two distinct phases are actually coexisting in the apparent coexistence region, we have made measurements of the surface potential at a single fixed temperature (20.1°C) for densities ranging from 4 to 416 molecules/ (10^4 \AA^2) . For this temperature we have previously found² the coexistence region to extend from 15 to 119 molecules/ (10^4 \AA^2) . The present work was stimulated by the fact that previous work⁴ on pentadecanoic acid has shown considerable variation of the surface potential with horizontal position above the film, indicating a heterogeneous mixture, but these measurements were not made in the density range which our surface-pressure measurements showed to be the region of coexistence between liquid and gaseous phases.

The measurements were made using the ionizing electrode method,¹ with a gold electrode backed by ²²⁶Ra in the air above the water surface, and an untreated platinum electrode in the water. The potential was measured by using a Keithley Model 153 microvoltammeter as a current null detector, and a simple 10-turn potentiometer and Hg cell to provide an opposing emf. Since the resistance of the ionized air gap between the air electrode, located ~2 mm above the surface, and the surface itself was ~ $10^9 \Omega$, careful guarding and shielding were required to eliminate leakage currents. The results were independent of the distance between

the air electrode and the water surface in the range from 0 to ~7 mm. The preparation of the trough and accessories as well as the water substrate were as described in our previous paper.² By leaving the air electrode in the experimental atmosphere of saturated water vapor for several days prior to making measurements, we were able to reproduce our results to within ± 1 mV. The measurements were made by cleaning the surface, measuring the potential of the clean surface, and then spreading a film of the desired density and measuring the resulting change in potential. The potential of the cleaned surface itself was stable to ± 2 mV for several hours, but was not reproducible from day to day. In order to examine the heterogeneity of a film, we used a gentle air stream to move the film about on the surface. Once a region of especially high or low potential had been moved under the electrode, the air stream was shut off and the potential was monitored for ~10 min.

The results of these measurements are summarized in Fig. 1, which shows the surface potential at various mean densities. Data points represented by a circle indicate that at that density no discernible variations in surface potential could be caused by moving the film about. In those density regions where variations existed, the data are represented by a vertical bar extending from the largest to the smallest potential observed at that density. The sign of the potential is considered positive if spreading the film causes the air electrode to become more positive with respect to the water. This corresponds to a dipole moment per unit area at the surface which is oriented from the surface toward the air. Even at densities as low as 4 molecules/ (10^4 \AA^2) we observed the potential to be positive by a few mV, *provided the surface was scrupulously cleaned*. Measurements made at low densities on inadequately cleaned surfaces gave negative values for the potential, which may explain such observations by other workers.⁵

As shown in Fig. 1, in the density range between that of the coexisting vapor and liquid the surface

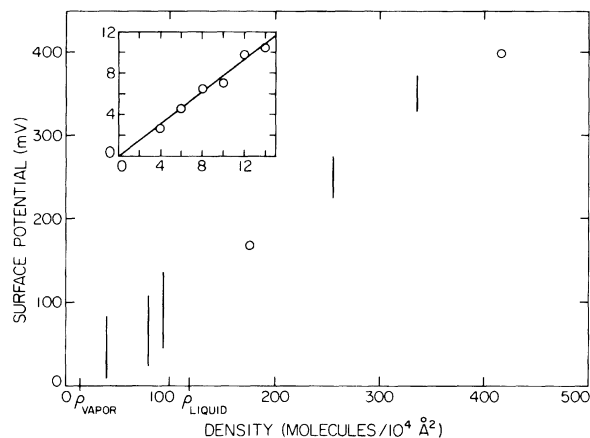


FIG. 1. Surface potential of a monomolecular film of pentadecanoic acid on a pH-2 water surface as a function of film density at 20.1 °C. The vertical bars show the maximum and minimum potentials observed at any given density, while data points represented by circles indicate that no variations were observed at that density. The inset shows the results obtained at low densities, and the densities of the coexisting liquid and vapor phases at 20.1 °C are also indicated.

potential exhibited very large variations. Since our results were not affected by the exact state of surface cleanliness, provided the surface was quite clean,² we feel that they offer further evidence for the simultaneous existence of two distinct phases on the surface. The gradual increase of both the minimum and maximum observed potential with average density would be expected if the two phases coexisted in patches with a size comparable to or smaller than that of the air electrode, which was 0.3 cm in diameter. As expected, no variations were observed at a mean density of 176 molecules/

(10^4 \AA^2) which exceeds the density of the liquid phase at this temperature. Variations were observed at higher densities but vanished upon further increase in density, as shown in Fig. 1. Presumably, this indicates the presence of another phase transition at these higher densities.

Surface chemists have often found it advantageous to consider the surface potential of a film in terms of the equivalent dipole moment per unit area required to generate the same change in work function. One may then obtain the effective contribution per molecule to this dipole layer. Although this involves the component of a dipole moment perpendicular to the surface, it is recognized that this moment includes not only the effect of the intrinsic dipole moment of the molecule, but the effects of each molecule on the structure of the water-air interface as well. With these limitations in mind, it is of interest to examine the way in which the effective dipole moment per molecule varies with density. As may be seen by the inset in Fig. 1, the potential depends linearly on density in the low-density limit. The effective normal component of the dipole moment per molecule in this region is 2.06×10^{-19} esu cm. At a density of 176 molecules/ 10^4 \AA^2 it is 2.52×10^{-19} esu cm, and at 416 molecules/ 10^4 \AA^2 it is 2.54×10^{-19} esu cm. At this density the average area per molecule is 24 \AA^2 which is essentially equal to the cross-sectional area of the molecule, and it is very likely that the molecules are oriented relative to the surface. Thus it appears that there is relatively little reorientation from the dilute gas region to quite high densities, or that reorientation has little effect upon the surface potential contribution per molecule.

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¹ See G. L. Gaines, Jr., *Insoluble Monolayers at Liquid-Gas Interfaces* (Wiley, New York, 1966), Chap. 3.

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⁴ W. D. Harkins and E. K. Fischer, *J. Chem. Phys.* **1**, 852 (1933).

⁵ M. Jean Guastalla, *C. R. Acad. Sci.* **224**, 1498 (1947).