

JonesRay Effect, Wettability, and ZetaPotential

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Citation: [The Journal of Chemical Physics](#) **14**, 462 (1946); doi: 10.1063/1.1724168

View online: <http://dx.doi.org/10.1063/1.1724168>

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Jones-Ray Effect, Wettability, and Zeta-Potential

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May 28, 1946

EXCEPT for an observation of Heydweiller¹ who noticed that chlorate solutions wetted the glass he used poorly, no consideration seems to have been given to the possibility that the presence of ions in solution may affect the angle of contact. In interpreting the Jones-Ray effect,² so far, perfect wettability of the capillary walls has been taken for granted. The explanation suggested by Langmuir³ appears to be in accord with a great deal of experimental evidence.⁴ However, it is difficult to reconcile his hypothesis with the Laplace equilibrium condition at the meniscus/film boundary in the limiting case of absolutely pure liquids where no difference of osmotic pressures can be thought of. An alternative view is here presented, namely that an increase of the wetting angle may be involved in the apparent decrease of surface tensions as found with minute concentrations of strong electrolytes.

The cylindrical capillary layer adjacent to a perfectly wetting meniscus is usually treated as if it were a "duplex film" of liquid in bulk. However, one should be aware of the fact that its vapor pressure is smaller than that of a hollow cylinder of liquid in mass of equal diameter whose vapor pressure equals that of a capillary film of twice the capillary radius. Therefore, the capillary film should be recognized as an "adsorbed phase."⁵ Accordingly, one should not conclude that its "surface tension" is equal to that of the liquid, or that its "interfacial tension" at the film/solid boundary is the same as that of the liquid/solid interface. It appears also questionable that the solubilities of electrolytes or non-ionic substances are the same in the capillary film as in the liquid, because the dielectric constants may be different, that of the film probably being smaller.

The following is based upon Gibbs' treatment of "Surfaces of Discontinuity between Solids and Fluids"⁶ which implies that the "surfaces of tension" coincide closely with the physical surfaces of the solids, no matter what the thickness of the adsorbed films, provided that the radii of curvature are very large in proportion to the film thickness.

According to Neumann's equation the "apparent sur-

face tension" of the liquid equals the difference of the vapor solid surface tension, σ' , and the liquid/solid interfacial tension, σ . Whatever the value of the contact angle, a change in capillary height will result from the adsorption of a third component and the desorption of solvent by which the difference of the tensions is altered:

$$d(\sigma' - \sigma) = -(\Gamma_2' - \Gamma_2)d\mu_2 - (\Gamma_3' - \Gamma_3)d\mu_3. \quad (1)$$

Here, the negative quantity of solvent adsorbed at the liquid/solid interface can be neglected in comparison to the excess adsorbed in the film. The excess of the third component in the film comprises the quantity adsorbed at the film/solid interface and the total amount dissolved in the film volume per unit area:

$$(c_3'/c_2')\Gamma_2'. \quad (2)$$

The molar potentials of solvent and solute are (approximately) correlated by the (Duhem) equation:

$$c_2 d\mu_2 + c_3 d\mu_3 = 0, \quad (3)$$

where c_2 and c_3 are the numbers of moles per unit volume. Equation (1), therefore, assumes the form:

$$d(\sigma' - \sigma) = \left[\Gamma_2' \left(\frac{c_3}{c_2} - \frac{c_3'}{c_2'} \right) - \Gamma_3' + \Gamma_3 \right] d\mu_3, \quad (4)$$

which for very small concentrations reduces further to:

$$d(\sigma' - \sigma) = (\Gamma_3 - \Gamma_3') d\mu_3. \quad (5)$$

Hence, in the range of minute concentrations, an increase or decrease in capillary height would solely depend on whether the excess of adsorbed solute is greater at the liquid/solid interface or at the film/solid interface.

Regarding the possibility that the dielectric constant of the film is smaller than that of the solvent in mass, the behavior of sugar solutions would appear as quite normal. In case of electrolytes, at first view, the same might be expected. However, Langmuir's⁷ theory of the potential distribution between parallel solid surfaces as a function of their distance seems to open an understanding of the reverse case.

There is also experimental evidence in favor of the present interpretation. The diffuse double layer in the vicinity of an insulator of high Z-potential is obviously of the same character as that of a highly polarized metal electrode in contact with an electrolyte solution. Now, the contact angles of gas bubbles attached to metal electrodes have been the subject of extensive studies by Frumkin and his co-workers⁸ who have established the fact that the contact angle decreases when the potential increases. Accordingly, it is logical to conclude that the Jones-Ray effect is caused by an increase of the wetting angle resulting from a decrease in the Z-potential at the solution/solid interface.

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