

Equations for the Pressure (Area) Relations (Isotherms) of Liquid Expanded and Intermediate Monolayers on Water

George Jura and William D. Harkins

Citation: *The Journal of Chemical Physics* **12**, 113 (1944); doi: 10.1063/1.1723914

View online: <http://dx.doi.org/10.1063/1.1723914>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/12/3?ver=pdfcov>

Published by the AIP Publishing

Articles you may be interested in

Monte Carlo computer simulation of spreading pressure-area isotherms of Langmuir monolayers of fatty-acid molecules

J. Chem. Phys. **115**, 6185 (2001); 10.1063/1.1395058

Mechanical properties of fatty acid monolayers on the water surface based on surface pressure relaxation and area creep measurements (abstract)

J. Rheol. **36**, 974 (1992); 10.1122/1.550327

The phases of insoluble monolayers: Comparison between the surface pressure-molecular area (A) diagram and shear modulus measurements

J. Chem. Phys. **78**, 4776 (1983); 10.1063/1.445277

Relation between Adsorption Isotherm and Adsorption Rate Equation

J. Chem. Phys. **25**, 1283 (1956); 10.1063/1.1743202

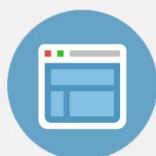
The Pressure-Volume-Temperature Relations of the Liquid, and the Phase Diagram of Heavy Water

J. Chem. Phys. **3**, 597 (1935); 10.1063/1.1749561



Re-register for Table of Content Alerts

Create a profile.



Sign up today!



cases one equation fits two different phases, but with very different values of the constants. It is found that the equations for insoluble films on water fit equally well for adsorbed films on solids.

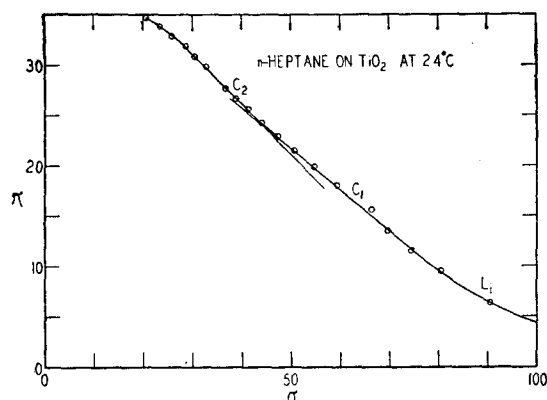


FIG. 2.

TWO CONDENSED PHASES IN FILMS (C₁ AND C₂) ON SOLIDS

The relation expressed by Eq. (1) or (2) is linear. When either of these is applied to films on solids it is often found that the plot obtained exhibits two straight lines such as to indicate the existence in the film on the solid of two condensed phases with a second-order transition, and thus an absence of a latent heat, between them (Figs. 1 and 2). The transition between the intermediate (L_i) and the condensed film (L_c) may be considered as of the third order.

Examples of this are found in films of propyl alcohol on barium sulfate or anatase (TiO₂), and of nitrogen on certain catalysts used in the petroleum industry, or on certain charcoals.

The only previously recognized phase on solids is the gaseous film.

Equations for the Pressure (π)-Area (σ) Relations (Isotherms) of Liquid Expanded and Intermediate Monolayers on Water

GEORGE JURA AND WILLIAM D. HARKINS
University of Chicago and Universal Oil Products Company,
Chicago, Illinois
February 9, 1944

IN earlier communications the writers have given equivalent equations for the isotherms of condensed films either adsorbed or spread on the surfaces of liquids or solids. These are

$$\pi = b - a\sigma, \quad (1)$$

$$\log \frac{f}{f_0} = B - \frac{A}{V^2} = B' - \frac{A'}{m^2} = \log \frac{p}{p_0}. \quad (2)$$

Here Eq. (1) is so simple that its form is obvious.

This is not at all true in the case of the liquid expanded or liquid intermediate phases on an aqueous subphase,

since no earlier equation which fits their behavior has ever been developed.

In this connection the well-known equation of Langmuir,¹ a simplified van der Waals equation, which is supposed to exhibit the pressure (π)-area (σ) relations of liquid expanded monolayers, may be considered. It is

$$(\pi - \pi_0)(\sigma - \sigma_0) = kT. \quad (3)$$

However, endeavors to fit this equation to any of the very large number of determinations in this laboratory of the pressure-area relations of the liquid expanded phase have shown that no equation of this type represents the data at all well.

Since the equations for the compressibilities (κ) of the expanded and intermediate phases are much simpler than those for the film pressures (π), our method of procedure is to obtain first the equation for the compressibility, where $\kappa = -(1/\sigma)(\partial\sigma/\partial\pi)_{T,p}$, and then to integrate the equation to obtain that for π.

A study of the data for the liquid expanded and intermediate films of insoluble materials on aqueous subphases has shown that the following equations for the compressibility represent adequately the experimental data:

(1) Liquid expanded phase:

$$\kappa = \frac{1}{a\sigma - b} \quad (4)$$

where the constants *a* and *b* have positive signs. On integration the π, σ relationship is found to be

$$\pi = c + a\sigma - b \ln \sigma. \quad (5)$$

(2) Intermediate phase:

$$\kappa = -a + (b/\sigma). \quad (6)$$

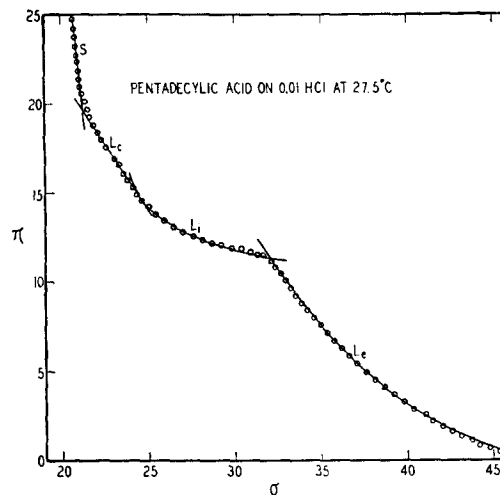


FIG. 1.

The constants *a* and *b* are again considered to be positive. The pressure-area relationship found on integration is

$$\pi = c - 1/a \ln (a\sigma - b). \quad (7)$$

At the present time these relationships are to be considered empirical. The only theoretical significance apparent at present is that obtained by comparing the compressibility to that of the condensed phase. Here the compressibility is known to be

$$\kappa = -a/\sigma. \quad (8)$$

The normal succession of phases, when the three appear by compression is (1) the expanded, (2) the intermediate, and (3) the condensed. The compressibilities of the film, in the same order, are $-(1/a\sigma - b)$, $-a + (b/\sigma)$, and $-a/\sigma$. Insufficient work has been done, as yet, to determine whether the constants a and b have theoretical significance. Figure 1 shows the application of the above equations to the liquid expanded and intermediate films of pentadecylic acid at 27.5° C on water.

¹ I. Langmuir, J. Chem. Phys. 1, 762 (1933).

The Existence of Expanded and Intermediate Phases in Films on Solids

GEORGE JURA AND WILLIAM D. HARKINS
University of Chicago and Universal Oil Products Company,
Chicago, Illinois
February 9, 1944

IN this communication it is shown that the equations developed for insoluble monolayers on water in the liquid expanded and intermediate phases are valid for certain films adsorbed on the surfaces of non-porous and porous solids. From this evidence the conclusion is reached that these two non-condensed phases exist in films on the surfaces of solids as well as on liquids. This conclusion is based on work with adsorbed films of butane on porous solids (catalysts) at 0° C. These exhibit even the second-order transition between the two phases. The pressure-area diagram for one of these solids is shown in Fig. 1.

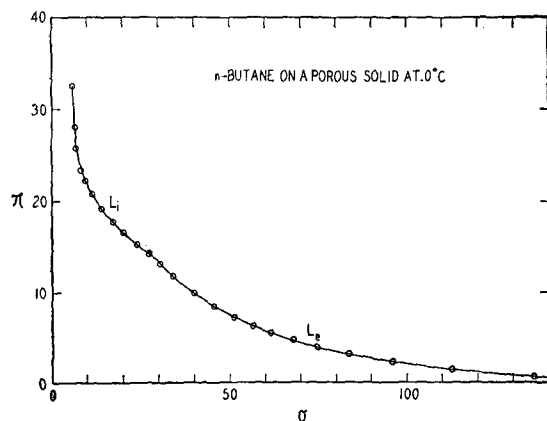


FIG. 1.

The equation obtained for the adsorption isotherm of the expanded phase, as obtained from Eq. (5) of the preceding paper, is

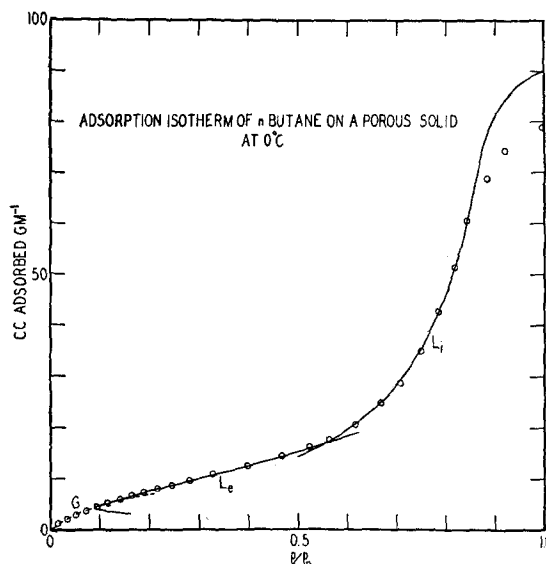


FIG. 2.

$$\log_{10} p = C + \frac{aA}{2.303B} \cdot \frac{1}{v^2} - \frac{b}{B} \cdot \frac{1}{v} \quad (8)$$

while that for the intermediate phase is

$$\log_{10} p = C + \frac{aA}{2 \times 2.303B} \cdot \frac{1}{v^2} - \frac{b}{a^2 AB} \log \frac{aA - bv}{v}. \quad (9)$$

In these equations p is the equilibrium pressure, v the volume of gas adsorbed per gram, a and b the constants in the compressibility equation,

$$A = 10^{18} \times 22,410 \Sigma / 6.023 \times 10^{23}, \text{ and } B = RT/22,410 \Sigma.$$

In the expressions for A and B , Σ is the specific area of the solid in $\text{cm}^2 \text{g}^{-1}$. The application of these equations to the adsorption data is shown in Fig. 2. Actually three phases are shown, the gaseous, the expanded, and the intermediate. The agreement between the observed and calculated values is well within experimental error except at very high pressures. Here the deviation is undoubtedly due to the fact that the pores are limiting the amount of material which is being adsorbed.

Thermodynamics of Heterogeneous Polymer Solutions

PAUL J. FLORY
Goodyear Research Laboratory, The Goodyear Tire and Rubber Company,
Akron, Ohio
February 11, 1944

THE equations derived by Huggins¹ and the writer² to represent the thermodynamics of polymer solutions take no account of the heterogeneity of the polymer. This limitation is of no consequence in the treatment of osmotic pressure, vapor pressure lowering, etc., in systems composed of a single polymer-containing phase, provided that the number average degree of polymerization is employed.