

Thermodynamics of Heterogeneous Polymer Solutions

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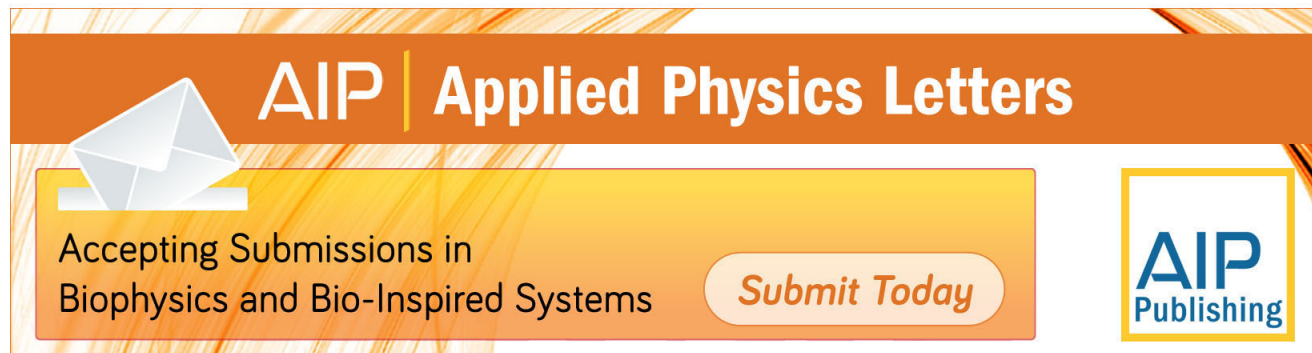
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At the present time these relationships are to be considered empirical. The only theoretical significance apparent at present is that obtained by comparing the compressibility to that of the condensed phase. Here the compressibility is known to be

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

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

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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.

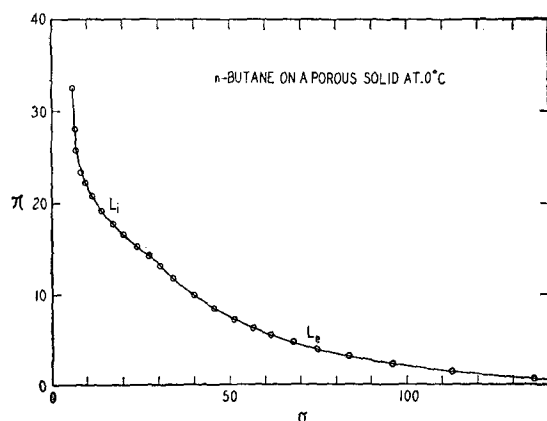


FIG. 1.

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

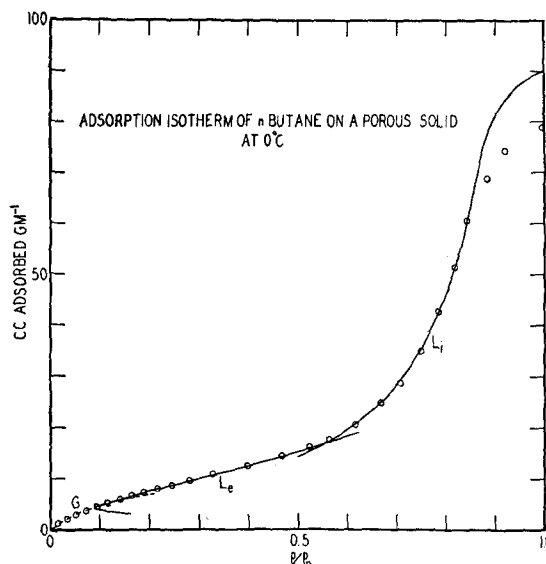


FIG. 2.

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

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

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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.

In dealing with solubility and fractional precipitation (or solution) of polymers composed of numerous species differing in molecular size, the above equations obviously are inadequate.

The previously employed statistical mechanical procedures can be readily applied to solvent-heterogeneous polymer systems. The following expression is derived for the entropy of mixing of n moles of solvent with N_1, N_2, N_3, \dots moles of polymer molecules of 1, 2, 3, \dots units, respectively, each existing initially as a pure component in which the molecules are in disordered configurations

$$\Delta S^* = -R[n \ln v_1 + \sum (N_x \ln v_x)], \quad (1)$$

where v_1 and v_x are the volume fractions of solvent and x -mer, respectively. Partial differentiations with respect to n and to N_x yield the partial molal entropies of the components. Combining these with van Laar partial molal heat of mixing terms, $\mu RT v_2^2$ and $\mu x RT (1 - v_2)^2$, the partial molal free energies

$$\Delta \bar{F}_1 = RT[\ln(1 - v_2) + (1 - 1/\bar{x}_n)v_2 + \mu v_2^2], \quad (2)$$

$$\Delta \bar{F}_x = RT[\ln v_x - (x - 1)(1 - v_2) + v_2(1 - x/\bar{x}_n) + \mu x(1 - v_2)^2] \quad (3)$$

are obtained, where v_2 is the volume fraction of all polymer species and \bar{x}_n is their number average number of units per polymer molecule.³ The precipitation of a polymer from solution occurs with the formation of two liquid phases,² one richer in the polymer constituent than the other. The higher polymers occur preferentially in the more concentrated phase (precipitate) which actually may consist largely of solvent.³ Analysis of solubility and fractionation of heterogeneous polymers requires the introduction of the conditions for equilibrium between the coexisting phases, i.e.,

$$\Delta \bar{F}_1 = \Delta \bar{F}_1', \quad (4)$$

$$\Delta \bar{F}_x = \Delta \bar{F}_x', \quad (5)$$

where the unprimed terms refer to the dilute phase and the primed terms to the more concentrated (precipitated phase). Substituting (3) in (5) there is obtained

$$v_x'/v_x = \exp(\alpha x) \quad (6)$$

where

$$\alpha = v_2(1 - 1/\bar{x}_n) - v_2'(1 - 1/\bar{x}_n') + \mu[(1 - v_2)^2 - (1 - v_2')^2], \quad (7)$$

assuming μ to be the same in both phases.

Equation (6) expresses the form of the partition of polymer species between the two phases as a function of their size x . However, the separation factor α is not an explicit function of independent variables. Complete analysis of the partition of a polymer of known distribution of species requires use of the following approximate equation, obtained from (2) and (4),

$$(v_2' - v_2)^2 / 12(1 - v_2' - v_2) \leq \frac{\alpha}{2}(v_2' + v_2) - v_2'/\bar{x}_n' + v_2/\bar{x}_n \quad (8)$$

and the necessary condition

$$\sum [v_x^0 e^{\alpha x} / (1 + r e^{\alpha x})] / \sum [v_x^0 / (1 + r e^{\alpha x})] = v_2' / v_2, \quad (9)$$

where v_x^0 is the initial volume of x -mer and r is the ratio of the volumes of the two phases.

These equations are not soluble in terms of the independent variables μ , the initial distribution (v_x^0 's), and total concentration. It is feasible, however, to substitute assumed values of r and α in (9) and in equations not included here for the number averages x_n and x_n' . Equation (8) can then be solved for v_2 and v_2' , and μ can be obtained from (7).

The application of these equations to solubility and fractionation of high polymers will be published in greater detail when time permits.

¹ M. L. Huggins, *J. Phys. Chem.* **46**, 151 (1942); *Annals N. Y. Acad. Sci.* **43**, 1 (1942); *Ind. Eng. Chem.* **35**, 216 (1943).

² P. J. Flory, *J. Chem. Phys.* **10**, 51 (1942).

³ The entropy expression (1), or its analog for a homogeneous polymer, fails to yield correct entropies in the region of dilute solutions. (Paper presented by the writer before the Pittsburgh Meeting of the American Chemical Society, September, 1943.) Huggins (reference 1) has shown that free energy expressions corresponding to (2) and (3) reproduce experimental data satisfactorily. It is necessary, however, to regard μ as an empirical parameter only part of which arises from the heat of mixing. Thus, although the theory is at fault in dilute solutions, Eqs. (2) and (3) should reproduce satisfactorily the actual free energies of the components throughout the concentration range.

Condensation and Supersaturation of Adsorbed Phases

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February 15, 1944

IT is well known that in the derivation of Langmuir's adsorption isotherm the interaction of neighboring adatoms has been neglected. Consequently, the equation of state of the monolayer corresponds to that of a compressed gas above its critical point. It is remarkable that this holds, no matter what the magnitude of the adsorption energy. This being so, the question naturally arises: How can the recently developed extensions of the simple Langmuir mechanism to the treatment of multilayers in the adsorption of vapors account for the final liquefaction of the adsorbate?

Let us write the Emmett-Brunauer-Teller¹ adsorption isotherm:

$$\Gamma = \Gamma_m c p P / (P - p) [P + (c - 1)p],$$

where Γ designates the surface density, Γ_m that of a complete monolayer, p the equilibrium, and P the saturation pressure of the adsorbate. Let us eliminate the surface density by applying Gibbs' equation:

$$-d\sigma = TRTd \log p$$

where σ is the sum of interfacial tension of the adsorbent and surface tension of the film. Hence integration gives the film pressure:

$$\sigma_0 - \sigma = F = \Gamma_m RT \log \frac{P + (c - 1)p}{P - p}.$$

So we have to conclude that the surface tension of the finally built-up, presumably liquid film would be negative.