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Application of Shereshefsky's Equation for the Determination of Solid Surface Dispersion Energy

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Summary A simple method for obtaining solid surface dispersion energies by measuring adsorption from solution and applying Shereshefsky's equation has been tested with experimental data from the literature on the adsorption of stearic acid from C_6H_6 solution on to mercury, iron, copper, and nickel giving results that compare favourably with those obtained by contact angle or by vapour phase adsorption measurements.

Shereshefsky,[1] on the basis of the thermodynamic considerations, has derived an equation which describes the surface tension of a binary solution in terms of its concentration, and Cotton[2] has shown that it is generally applicable. For a binary solution with an insoluble solid phase, the equation is expressed by

$$\frac{N_2}{\sigma_{1s} - \sigma} = \frac{1}{\sigma_{1s} - \sigma_{2s}} e^{-\Delta F12s/RT}$$
$$+ \frac{N_2}{\sigma_{1s} - \sigma_{2s}} (1 - e^{-\Delta F12s/RT}) \qquad (1)$$

where $\Delta F_{12s} = N_A(\sigma_{1s} - \sigma_{2s})A_{2s}/t$. N_2 is the solute mole fraction; σ, σ_{1s}, and σ_{2s} are the interfacial tensions between the solution and solid, between the pure solvent and solid, and between the pure solute and solid, respectively; A_{2s} is the area occupied by a solute molecule; t is the molecular thickness of the adsorbed layer; T is absolute temperature; N_A is Avogadro's number; and R is the gas constant. Accordingly, when $N_2/(\sigma_{1s} - \sigma)$ is plotted versus N_2, a straight line should result, and

$$(\text{slope}) = b = \frac{1}{\sigma_{1s} - \sigma_{2s}} (1 - e^{-\Delta F12s/RT}) \qquad (2)$$

$$(\text{intercept}) = a = \frac{1}{\sigma_{1s} - \sigma_{2s}} e^{-\Delta F12s/RT} \qquad (3)$$

$$\sigma_{1s} - \sigma_{2s} = \frac{1}{a + b} \qquad (4)$$

$$\Delta F_{12s} = RT\ln(b/a + 1) = (\sigma_{1s} - \sigma_{2s})A_{2s}/t \qquad (5)$$

When boundaries defining the interfacial region between a solid and a binary solution are such that the Gibbs surface excess concentration of the solvent is zero, then[3]

$$\sigma_{1s} - \sigma = -RT\int_0^{a_2} \Gamma_2 \mathrm{dln}(a_2) \qquad (6)$$

where Γ_2 is the Gibbs surface excess of concentration of the solute, and a_2 is the activity of the solute. For dilute solutions, mole fractions can be substituted for activities, and Γ_2 can be obtained by measuring adsorption through the change in concentration of the solution in contact with the solid and applying Guggenheim and Adam's equation.[4] Accordingly, if adsorption from a binary solution on to a solid as a function of concentration is measured, $\sigma_{1s} - \sigma_{2s}$, ΔF_{12s}, and A_{2s}/t can be obtained by applying Shereshefsky's equation.

Fowkes[5] has shown that the interfacial tension, i.e. the energy required to create the interface, between a liquid phase (i) and a solid phase (s) is given by

$$\sigma_{ls} = \sigma_l + \sigma_s - 2(\sigma_l^d \sigma_s^d)^{\frac{1}{2}} \qquad (7)$$

where σ_{ls} is the interfacial tension between the pure liquid and the solid; σ_l and σ_s is the surface tension of the pure liquid and of the pure solid, respectively; and σ_l^d and σ_s^d are, respectively, the interaction energy due to London dispersion forces of the liquid and of the solid at the interface.

For two mutually soluble liquids, equation (7) applies to

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both. If the two resulting equations are simultaneously solved for σ_s^d by eliminating σ_S, equation (8) is obtained.

$$\sigma_s^d = \tfrac{1}{4}\left[\frac{(\sigma_1 - \sigma_2) - (\sigma_{1s} - \sigma_{2s})}{(\sigma_1^d)^{\frac{1}{2}} - (\sigma_2^d)^{\frac{1}{2}}}\right]^2 \qquad (8)$$
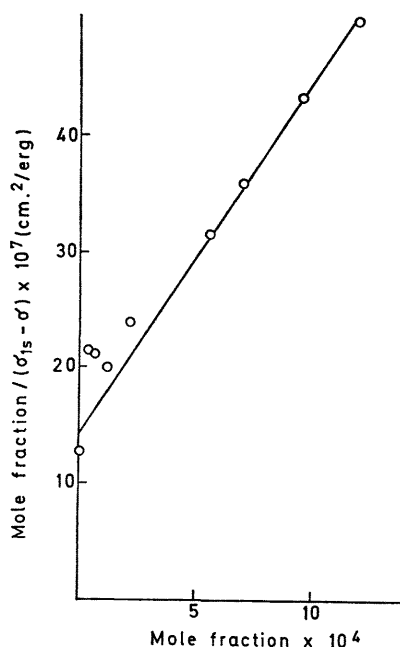

FIGURE 1. _Mole fraction divided by $\sigma_{1s} - \sigma$ vs. mole fraction for stearic acid in C_6H_6 against mercury._

The stearic acid surface excess of concentration on mercury was plotted _versus_ the logarithm of solution concentration, and the resulting curve was integrated in data point intervals by Gaussian quadratures. The stearic acid surface excess of concentration on iron, copper, and
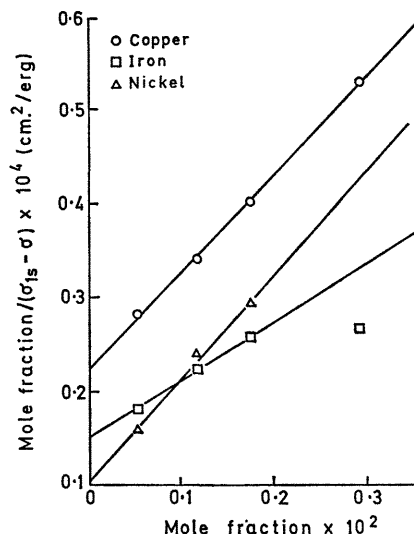

FIGURE 2. _Mole fraction divided by σ_{1s}!—$[\sigma$ vs. mole fraction for solutions of stearic acid in C_6H_6 against various metal powders._

nickel was least-square fitted to fourth-order polynomials which were then integrated. The integration results, $\sigma_{1s} - \sigma$, were least-square fitted to Shereshefsky's equation

Surface constants for mercury, iron, copper, and nickel obtained by adsorption of stearic acid from benzene solution measurements

Surface			$\sigma_{1s} - \sigma_{2s}$ (erg/cm.^{2})	$\Delta F_{12s} \times 10^{-9}$ (erg/mole)	A_{2s} (Å^2)	t	σ_s^d (erg/cm.^{2})	σ_s^d (ref. 5) (erg/cm.^{2})
Mercury	..	..	330	190	9·5	2	—	200
Iron	..	..	121	207	28·0	1	107	98
Copper	..	..	95	157	27·0	1	66	60
Nickel	..	..	70	173	42·0	$\frac{1}{2}$	36	—
			(103)				(78)	

For solid surfaces, $(\sigma_1^d)^{\frac{1}{2}} - (\sigma_2^d)^{\frac{1}{2}}$ is unique. Hence, if the interfacial tension of the binary solution as a function of concentration is determined against mercury, a metal for which σ_s^d is known, $(\sigma_1^d)^{\frac{1}{2}} - (\sigma_2^d)^{\frac{1}{2}}$ can be calculated by using Shereshefsky's equation in conjunction with equation (8). However, equation (8) was derived for pure liquid phases in contact with the solid phase which is equivalent to monolayer interaction, and multilayer formation is possible for some systems. Accordingly, equation (8) requires that the apparent value of $\sigma_{1s} - \sigma_{2s}$ as determined by Shereshefsky's equation be divided by the molecular thickness of the adsorbed layer, t. Therefore, equation (8) expresses σ_s^d, the solid surface dispersion energy, as a function of parameters easily obtained from surface tension and adsorption from solution measurements.

Data by Grant[6] on the adsorption of stearic acid from C_6H_6 solution on to mercury and data by Greenhill[7] for the adsorption of stearic acid from C_6H_6 on to iron, copper, and nickel powders were used to test the equations.

(see Figures 1 and 2). Equations (2)—(5) were used to calculate $\sigma_{1s} - \sigma_{2s}$, ΔF_{12s}, and A_{2s} for each surface. The molecular layer thickness, t, was calculated by assuming the molecular area of stearic acid to be 20·5 Å^2 as determined by Langmuir.[8] Results are shown in the Table. For the stearic acid–C_6H_6–mercury system, $\sigma_{1s} - \sigma_{2s} = 330$ erg/cm^2, $\sigma_s^d = 200$ erg/cm.^{2};[5] $\sigma_1(C_6H_6) = 28\cdot88$ erg/cm.^{2};[9] and σ_2 (stearic acid at its m.p.) $= 28\cdot90$ erg/cm.^{2},[10] and therefore t = 2, and since $\sigma_1 \approx \sigma_2$, $(\sigma)_1^{d\frac{1}{2}} - (\sigma)_2^{2\frac{1}{2}} = -5\cdot8$ (erg/cm^2)$^{\frac{1}{2}}$.

From the Table it is seen that A_{2s} and σ_s^d for iron and for copper are in good agreement with Fowkes' values. In the case of nickel, A_{2s} was 41 Å^2 corresponding to a non-integer value for t which is physically impossible, and σ_s^d was 36 erg/cm^2 which is too low. This suggests that the reported specific surface area of the nickel powder was too high. ΔF_{12s}, however, is independent of the specific surface area of the adsorbent. The values in parentheses for nickel (Table) were calculated using ΔF_{12s} and assuming monolayer adsorption and that the area of the stearic acid

molecule to be the same as was found for iron and for copper. The results are reasonable inasmuch as σ_s^d for nickel was expected to be between that for iron and for copper.

On the basis of this available evidence, the application of Shereshefsky's equation for the determination of solid surface dispersion energy by liquid phase adsorption is valid. The technique is attractive because the solids can be in the form of powders which are easily obtained and readily purified. Moreover, adsorption from solution can be accurately ascertained by simple solution concentration measurements, i.e. interferometry, refractometry, spectroscopy, etc., or by radioisotope tracer techniques.

[1] J. L. Shereshefsky, J. Colloid Interfacial Sci., 1967, 24, 317.
[2] D. J. Cotton, J. Phys. Chem., 1969, 73, 270.
[3] J. W. Gibbs, Trans. Connecticutt Acad., 1874, 3, 439.
[4] E. A. Guggenheim and N. K. Adam, Proc. Roy. Soc., 1933, A, 139, 218.
[5] F. M. Fowkes, Ind. and Eng. Chem., 1964, 56, 40.
[6] W. H. Grant, Ph.D. Thesis, Howard Univ., Washington, D.C., 1968.
[7] E. B. Greenhill, Trans. Faraday Soc., 1949, 45, 625.
[8] I. Langmuir, J. Amer. Chem. Soc., 1917, 39, 1848.
[9] 'International Critical Tables,' McGraw–Hill, New York, 1928, vol. IV, p. 454.
[10] K. W. Hunter and O. Maase, J. Amer. Chem. Soc., 1929, 51, 153.