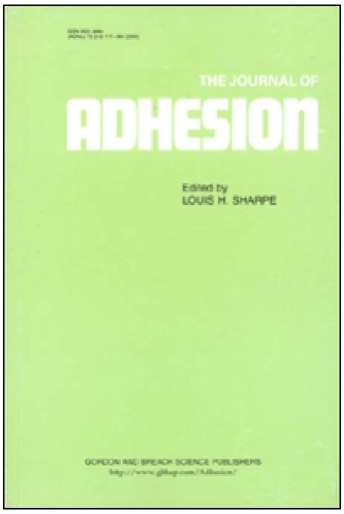
This article was downloaded by:
On: *22 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



The Journal of Adhesion

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Surface Chemistry and Adhesion- A Review of Some Fundamentals

J. R. Huntsberger[a]

[a] Plastics Department. Experimental Station, E. I. du Pont de Nemours & Company, Inc., Wilmington, Delaware, U.S.A.

To cite this Article Huntsberger, J. R.(1976) 'Surface Chemistry and Adhesion- A Review of Some Fundamentals', The Journal of Adhesion, 7: 4, 289 — 299

To link to this Article: DOI: 10.1080/00218467608075060

URL: http://dx.doi.org/10.1080/00218467608075060

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

J. Adhesion 1976, Vol. 7, 289–299

Printed in Scotland

Surface Chemistry and Adhesion—A Review of Some Fundamentals

J. R. HUNTSBERGER

E. I. du Pont de Nemours & Company, Inc., Plastics Department, Experimental Station, Wilmington, Delaware 19898, U.S.A.

(*Received May 1, 1975*)

A critical review of some fundamentals of surface chemistry revealed several areas in which current interpretations of data or interrelationships are erroneous or misleading.

Correct forms of fundamental equations interrelating surface energies, equilibrium contact angles and adhesion are given and plotted in a convenient, illuminating, dimensionless form. These curves provide a basis for comparing some recently published empirical equations with the fundamental ones showing that discrepancies result from changing values of the interaction parameter ϕ.

A review of recent work indicates we might profitably re-emphasize surface chemistry and re-examine interfacial interactions and their relationships to adhesion.

Adhesive performance is much better understood than it was 10 years ago. This progress has come largely from work on viscoelasticity and fracture or continuum mechanics giving quantitative relationships between applied stresses and bond failure, and from work showing that performance may be controlled by mechanical responses of thin interfacial regions that differ chemically or structurally from the bulk phases in adhesive joints.

This has provided rational approaches for understanding and improving performance but has not helped when solutions for problems require stronger interfacial interactions.

This paper presents many of the fundamental relationships in the dimensionless form used by Good[1] for graphing interfacial tension vs. γ_{LV}/γ_{SO}. These are especially convenient, make inter-relationships easy to discern, and lead to some interesting specific values.

Presenting these curves and making critical judgments about some of the pertinent earlier work are the sole reasons for this paper. There is no intent nor implication that this is a comprehensive review, and no such inference is warranted.

What follows is based on the premise that the interaction parameter ϕ makes Eq. (1) exact.

$$W_{\mathrm{adh}} = 2\phi(\gamma_1\gamma_2)^{\frac{1}{2}} \tag{1}$$

where γ_1 and γ_2 are the surface tensions of materials of Phase 1 and Phase 2, respectively, in equilibrium with their own vapors only.

Any *calculated* value of ϕ on the other hand is considered an *estimate* of ϕ. The quality of such estimates undoubtedly varies from system to system.

The interaction parameter can be expressed as a product of two factors.[1]

$$\phi = \phi_a\phi_r \tag{2}$$

ϕ_a accounts for departures from ideality in intermolecular attractions and ϕ_r accounts for departures from regularity in interfacial separations.

The importance of variations of ϕ_r has been dismissed frequently (e.g., Ref. 1) on the premise that only when differences between the average intermolecular separations of the phases are large will ϕ_r be significantly less than unity. This is the result of assuming that the interfacial separation $\bar{r}_{12}$ is the arithmetic mean of the average intermolecular separations of the individual phases $\bar{r}_{11}$ and $\bar{r}_{22}$.

This assumption seems unwarranted, especially when polymers comprise at least one of the phases. The configurations of polymer molecules at an interface make it highly probable that effective mean interfacial separations are appreciably greater than the arithmetic mean based on segment volumes.

As a conservative estimate, if $\bar{r}_{11}$ for one phase were 20% larger than $\bar{r}_{22}$ for the other and the effective mean interfacial separation were equal to $\bar{r}_{11}$, ϕ_r would be only 0.83 and the work of adhesion would be 16% less than that calculated using $\phi_r = 0.99$ (based on the arithmetic mean assumption for the value of $\bar{r}_{12}$). For this same example the maximum or critical stress would be 28% less than that calculated using $\phi = 0.99$.

In reality discrepancies may frequently be greater than these.

Wu[3] found better agreement between measured values of γ_1, γ_2 and γ_{12} and values for ϕ_a calculated using harmonic means rather than geometric means. There is no satisfactory theoretical basis for this. Harmonic means lead to smaller values for work of adhesion and larger values for γ_{12} when $\gamma_1 \neq \gamma_2$. These energies are highly dependent on the values of ϕ and it seems likely that the apparent better agreement using harmonic means was due in reality to unrecognized and unaccounted for decreases in ϕ_r associated with polymers.

The molecular density at interfaces and the influence of molecular density on mean interfacial separations is in fact the most important single factor in determining surface and interfacial tensions. This is suggested for example by the relationship between surface tension and parachor which shows γ is directly proportional to the fourth power of the density. Hoernshemeyer[4] showed that the low surface energies of fluoropolymers are due mainly to their low molecular surface densities rather than the character of the attractive forces.

It is clear that close packing of surface layers can diminish interfacial interactions *only* when increasing packing diminishes intermolecular penetration into a surface layer. A macroscopic analogy is provided by the influence of surface roughness on contact angle hysteresis. When $\theta > 90°$ increasing roughness increases advancing contact angles, but when $\theta < 90°$ increasing roughness decreases advancing angles.

There are several fundamental relationships which are the basis for using contact angle equilibria for making inferences concerning adhesion. These include:

$$\gamma_{SL} = \gamma_{SO}+\gamma_{LV}-2\phi(\gamma_{SO}\gamma_{LV})^{\frac{1}{2}} \tag{3}$$

$$\gamma_{SV}-\gamma_{SL} = \gamma_{LV}\cos\theta \tag{4}$$

$$\gamma_{SO}-\pi_e = \gamma_{SV} \tag{5}$$

$$\pi_{SL}-\pi_e = \gamma_{LV}\cos\theta \tag{6}$$

$$\pi_{SL} = \gamma_{SO}-\gamma_{SL} \tag{7}$$

$$\gamma_{SO}-\pi_e-\gamma_{SL} = \gamma_{LV} \text{ when } \theta = 0 \tag{8}$$

In these equations γ_{SO} and γ_{LV} are values for the surface tensions of the solid and liquid, respectively, in equilibrium with their own vapours. The equilibrium spreading pressure of the vapour on the solid is π_e, and π_{SL} is the equilibrium spreading pressure of the liquid on the solid.

Equation (8) is a statement of Antonow's Rule at equilibrium. This was shown to be valid by Johnson and Dettre.[5]

In general, the initial spreading coefficients in three phase systems are defined by expressions of the form:

$$S_{2/13} = \gamma_{13}-\gamma_{12}-\gamma_{23} \tag{9}$$

$$= W_{\text{adh }12}+W_{\text{adh }23}-W_{\text{adh }13}-2\gamma_{2V} \tag{10}$$

where $S_{2/13}$ is the coefficient for Phase 2 spreading along the 13 interface.

For the special case where Phase 3 is vapor:

$$S_2/_{13} = W_{\text{adh }12}-2\gamma_{2V} \tag{11}$$

The following special values are obtained from the fundamental equations:

at $\theta = 0$, $S = 0$ (equilibrium coefficient)

at $\theta = 90°$, $\pi_{SL} = \pi_e$

Plotting these relationships in a dimensionless form as ratios with respect to γ_{SO} provides some interesting insights.

The work of adhesion as W_{adh}/γ_{SO} is plotted *vs* γ_{LV}/γ_{SO} in Figure 1. Note that the work of adhesion increases monotonically with increasing γ_{LV}.

The interfacial tension γ_{SL}/γ_{SO} is plotted *vs* γ_{LV}/γ_{SO} in Figure 2. The values for γ_{SL}/γ_{SO} exhibit minima at $\gamma_{LV}/\gamma_{SO} = \phi^2$. The minimum values for $\gamma_{SL}/\gamma_{SO} = (1-\phi^2)$. This was shown earlier by Good.[1]

The spreading pressure of the liquid on the solid π_{SL}/γ_{SO} is plotted in Figure 3. The initial spreading coefficient S_i/γ_{SO}, and the equilibrium spreading coefficient S/γ_{SO} are plotted in Figures 4 and 5.

From Figures 3 to 5 and Eqs. (1), (3), (5) and (7) the following relationships are clear:

$$W_{adh}-\gamma_{LV} = \pi_{SL}$$

$$W_{adh}-2\gamma_{LV} = S_i$$

$$W_{adh}-2\gamma_{LV}-\pi_e = S$$

When $\theta = 0$ π_{SL}/γ_{SO} exhibit maxima at $\gamma_{LV}/\gamma_{SO} = \phi^2$, $S = 0$ and $\pi_e = S_i$. Maxima for the S_i/γ_{SO} curves occur at $0.25\ \phi^2$. The maximum values for S_i/γ_{SO} and consequently also for π_e/γ_{SO} are equal to $0.5\ \phi^2$.

The plots of $\phi(\gamma_{LV}/\gamma_{SO})^{\frac{1}{2}}$ and $\phi(\gamma_{SO}/\gamma_{LV})^{\frac{1}{2}}$ in Figure 6 show the failure locus for *reversible* separation. When both values are <1, interfacial failure

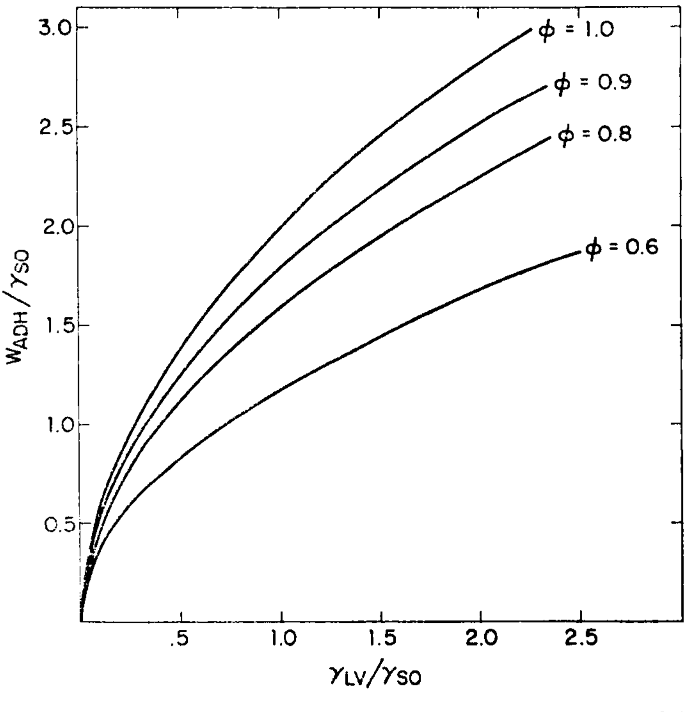


FIGURE 1 Work of adhesion/γ_{SO} *vs* γ_{LV}/γ_{SO} (for various values of ϕ).

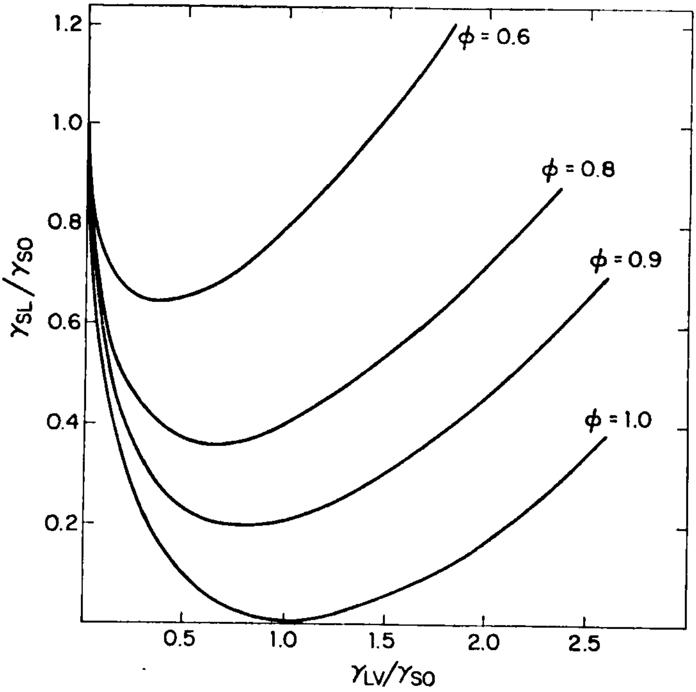


FIGURE 2 Interfacial tension (γ_{SL}/γ_{SO} *vs* γ_{LV}/γ_{SO} (for various values of ϕ).

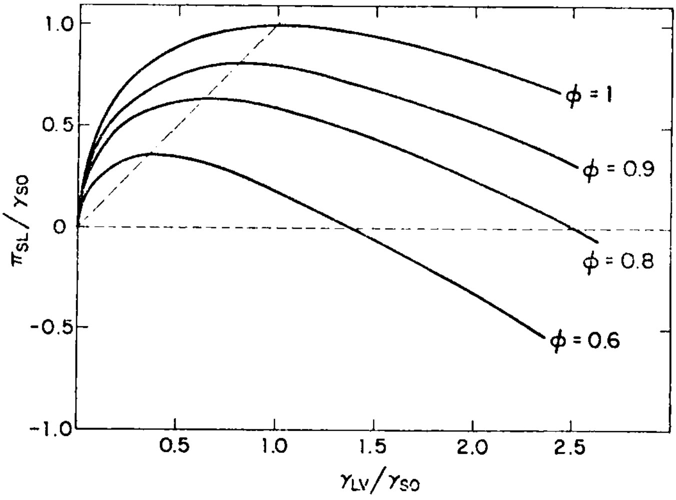


FIGURE 3 Spreading pressure of liquid on the solid (π_{SL})/γ_{SO} *vs* γ_{LV}/γ_{SO} (for various values of ϕ). $\pi_{SL} = \gamma_{SO} - \gamma_{SL}$; $\pi_{SL} = W_{ADH} - \gamma_{LV}$.

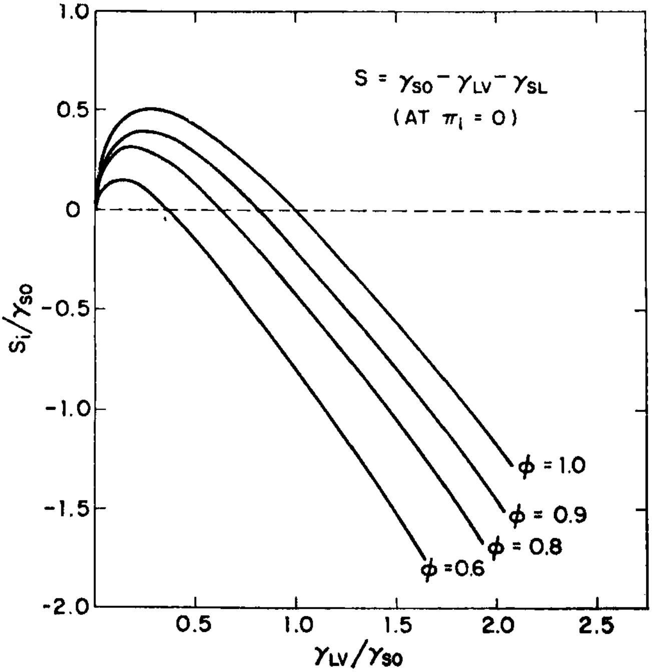


FIGURE 4 Init. spreading coefficient $(S_i)/\gamma_{SO}$ *vs* γ_{LV}/γ_{SO} (for various values of ϕ).

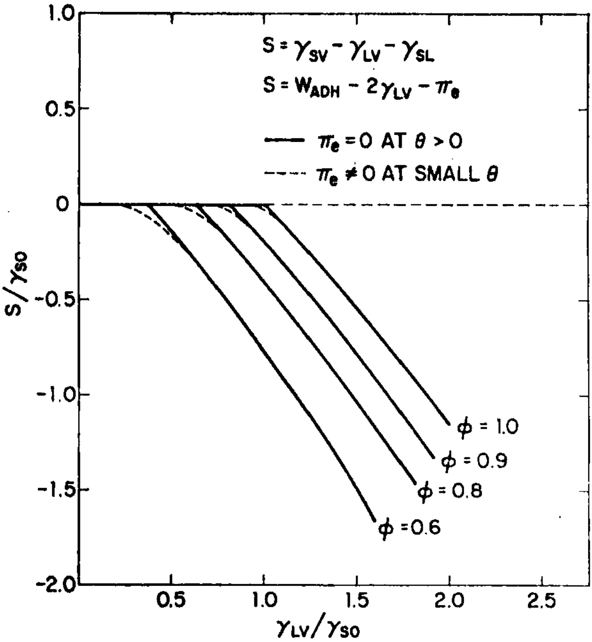


FIGURE 5 Equilibrium spreading coefficient S/γ_{SO} *vs* γ_{LV}/γ_{SO} (for various values of ϕ).

is predicted. While these criteria are only for reversible separation, recall that when ϕ becomes appreciably less than unity the critical stresses usually diminish more rapidly than the interfacial energies, and for samples with only small flaws or voids in the bulk phases the probability of interfacial separation is greatly increased. There is no reason to consider interfacial separation a rare or unlikely event.

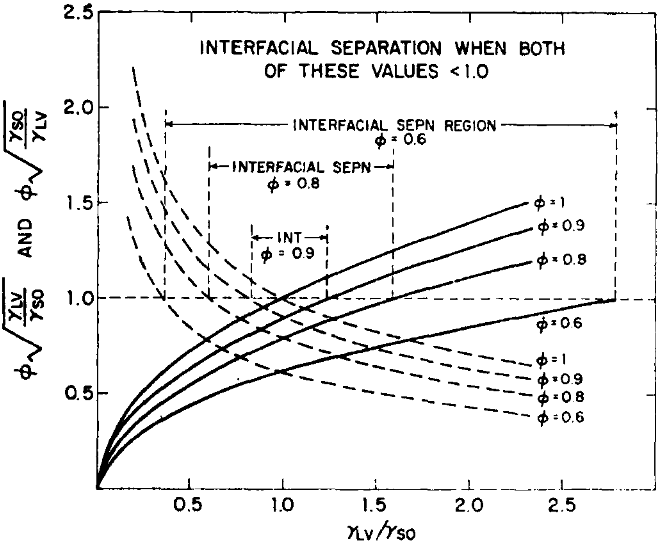


FIGURE 6 Failure criteria for reversible separation (at various values for ϕ). — = $\phi\left(\frac{\gamma_{LV}}{\gamma_{SO}}\right)^{\frac{1}{2}}$; - - - = $\phi\left(\frac{\gamma_{SO}}{\gamma_{LV}}\right)^{\frac{1}{2}}$.

In Figure 7 cos θ is plotted *vs* the dimensionless γ_{LV}/γ_{SO}. These curves represent the theoretical basis for Zisman plots of cos θ *vs* γ_{LV}. Figure 8 shows a Zisman plot for various liquids on poly(ethylene). Finite spreading pressures of the test liquids at low θ cause the curve to approximate a straight line in this region and also lead to values for γ_c ~3 dynes less than the value for γ_{SO} reported by others.[6,7,8] The approximately linear form of the data at higher θ and higher γ_{LV}/γ_{SO} is due to changes in ϕ for interactions between the liquids and poly(ethylene). The line Z in Figure 8 was drawn using Zisman's value for b,[9] in the equation:

$$\cos\theta = 1 + b(\gamma_c - \gamma_{LV}) \tag{12}$$

Zisman uses Eq. (12) and

$$W_{adh} = \gamma_{LV}(1 + \cos\theta) \tag{13}$$

to obtain:

$$W_{adh} = (2 + b\gamma_c)\gamma_{LV} - b\gamma_{LV}^2 \tag{14}$$

which is the equation for a parabola.

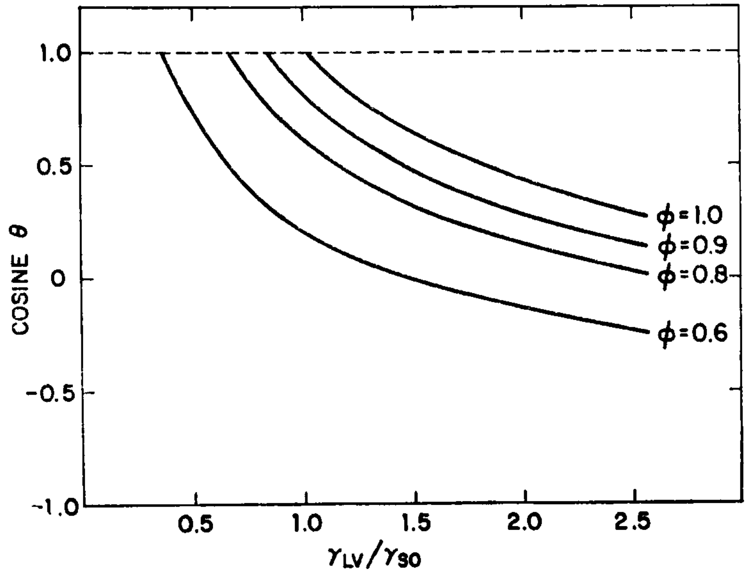


FIGURE 7 Cosine θ *vs* γ_{LV}/γ_{SO} (for various values of ϕ).

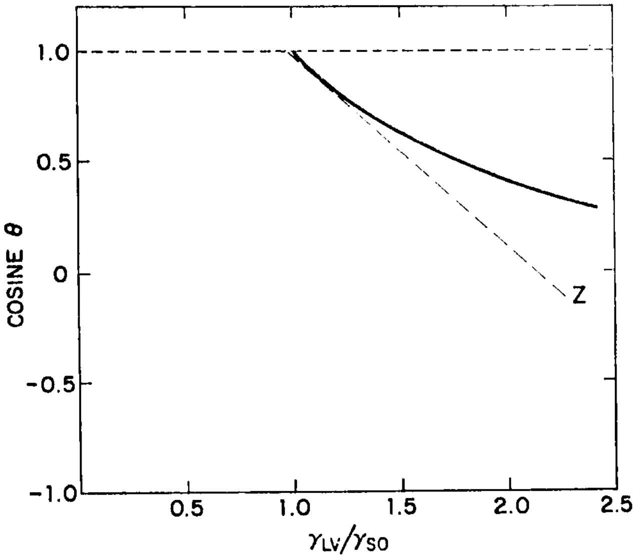


FIGURE 8 Cosine θ *vs* γ_{LV}/γ_{SO}. The dashed line Z is a plot corresponding to cos $\theta = 1+b\ (\gamma_C-\gamma_{LV})$ and using Zisman's value for b.

In Figure 9 Zisman's data are plotted on the curves for W_{adh}/γ_{SO} *vs* γ_{LV}/γ_{SO}. It is evident that the parabolic form simply reflects the diminishing values for the interaction parameter ϕ. Zisman recognized this as an empirical equation, and in the light of subsequent clarification Eq. (14) does not appear to be of any practical value and is subject to misinterpretation.

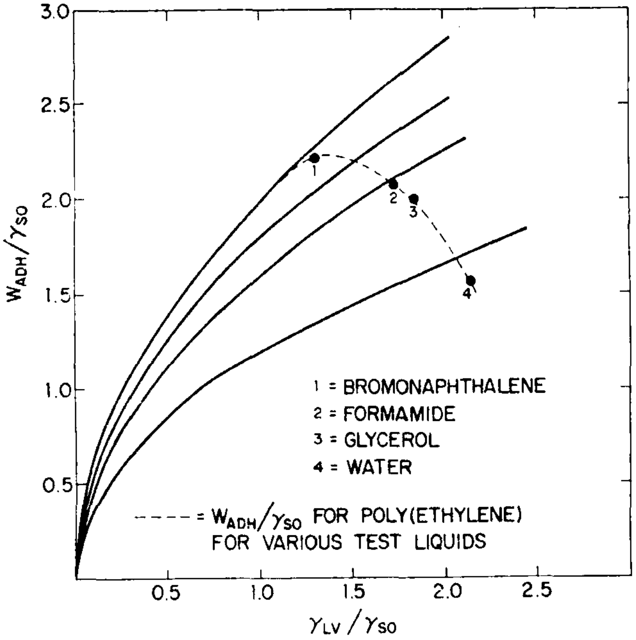


FIGURE 9 W_{ADH}/γ_{SO} *vs* γ_{LV}/γ_{SO} (for various values of ϕ).

Another equation bearing a resemblance to Eq. (14) was proposed recently by Neumann, Good, Hope and Sejpal[10]:

$$\gamma_{LV}\cos\theta = a\gamma_{LV}^2 + b\gamma_{LV} + c \qquad (15)$$

Curves based on Eq. (15) were plotted as $\gamma_{LV}\cos\theta$ *vs* γ_{LV}. From Eq. (6) we see that these curves bear the same relationship to the π_{SL}/γ_{SO} curves of Figure 3 that the Zisman curves had with Figures 1 and 7. That is, the π_{SL}/γ_{SO} (minus π_e/γ_{SO}) curves are the theoretical basis for the empirical N, G, H and S curves. This is shown in Figure 10. Here again the departure of the empirical curves reflects diminishing values of ϕ with increasing γ_{LV}/γ_{SO} and suggests that Eq. (15) has no special value.

N, G, H and S used the intercept of the curves with the 45° line to arrive at a value $(\gamma_{LV})^*$ which is in fact identical to Zisman's long established γ_c. These authors made unwarranted and highly restrictive assumptions ($\pi_e = 0$ at $\theta \geqslant 0$, and $(\gamma_{SL})^* = 0$ where $(\gamma_{SL})^*$ is the interfacial tension between the solid and liquid at $\gamma_{LV} = (\gamma_{LV})^*$). This latter assumption is valid only when $\phi = 1$ *and* $\gamma_{LV} = \gamma_{SO}$. An error fatal to their further argument was caused by substituting $(\gamma_{SV})^* = \gamma_c$ into Eq. (6) obtaining:

$$\phi = \frac{\gamma_c + \gamma_{LV} - \gamma_{SL}}{2(\gamma_c \gamma_{LV})^{\frac{1}{2}}} \tag{16}$$

instead of using the correct form based on $\gamma_c = \phi^2 \gamma_{SO}$:

$$\phi^2 = \frac{\gamma_c}{2(\gamma_c \gamma_{LV})^{\frac{1}{2}} + \gamma_{SL} - \gamma_{LV}} \tag{17}$$

They used Eq. (16) and values for γ_{SL} obtained using Eq. (4) to determine ϕ as a function of γ_{SL} and reported

$$\phi = 1 - 0.0075\,\gamma_{SL} \tag{18}$$

Since γ_c is itself a function of ϕ ($\gamma_c = \phi^2 \gamma_{SO}$) it is clear that Eq. (16) cannot lead to correct values.

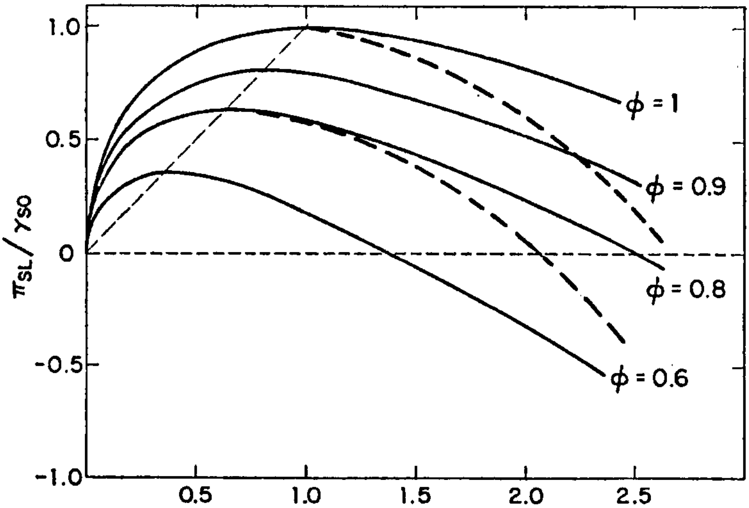


FIGURE 10 Spreading pressure of liquid on the solid $(\pi_{SL})/\gamma_{SO}$ *vs* γ_{LV}/γ_{SO} (for various values of ϕ). $\pi_{SL} = \gamma_{SO} - \gamma_{SL}$; $\pi_{SL} = W_{ADH} - \gamma_{LV}$.

It can be easily shown from the fundamental relationships that $d\phi/d\gamma_{SL}$ is linear only at constant γ_{LV}/γ_{SO}, and that the slope varies with changes in γ_{LV}/γ_{SO}. The slopes which would correspond to the incorrect value 0.0075 in Eq. (18) range over a broad region of γ_{LV}/γ_{SO} values from 2× to 10× the value from that equation.

It is unfortunate that the value for ϕ given in Eq. (18) was used as the basis for the Sell–Neumann Equation[11]:

$$\cos\theta = \frac{(0.015\gamma_{SO} - 2)(\gamma_{SO}\gamma_{LV})^{\frac{1}{2}} + \gamma_{LV}}{\gamma_{LV}[0.015(\gamma_{SO}\gamma_{LV})^{\frac{1}{2}} - 1]} \tag{19}$$

It follows that Eq. (19) also is not valid.

Eq. (19) was criticized earlier by Phillips and Riddiford.[12]

References

1. R. J. Good, *Ind. Eng. Chem.* **62,** 54 (1970).
2. L. A. Girifalco and R. J. Good, *J. Phys. Chem.* **61,** 904 (1957).
3. S. Wu, *J. Pol. Sci., Part C* **34,** 19 (1971).
4. D. Hoernshemeyer, *J. Phys. Chem.* **20,** 2628 (1966).
5. R. E. Johnson, Jr. and R. B. Dettre, *J. Coll. and Int. Sci.* **21,** 610 (1966).
6. H. W. Starkweather, Jr. *SPE Transactions* **5,** 1 (1965).
7. R. J. Roe, *J. Phys. Chem.* **69,** 2808 (1965).
8. S. Wu, *J. Coll. and Int. Sci.* **31,** 153 (1969).
9. W. A. Zisman, *Ind. Eng. Chem.* **55,** 19 (1963).
10. A. W. Neumann *et al., J. Coll. and Int. Sci.* **49,** 291 (1974).
11. P. J. Sell and A. W. Neumann, *Z. Phys. Chem.* **47,** 20 (1965).
12. A. C. Riddiford, *Wetting.* S.C.I. Monograph No. 25 (1967).