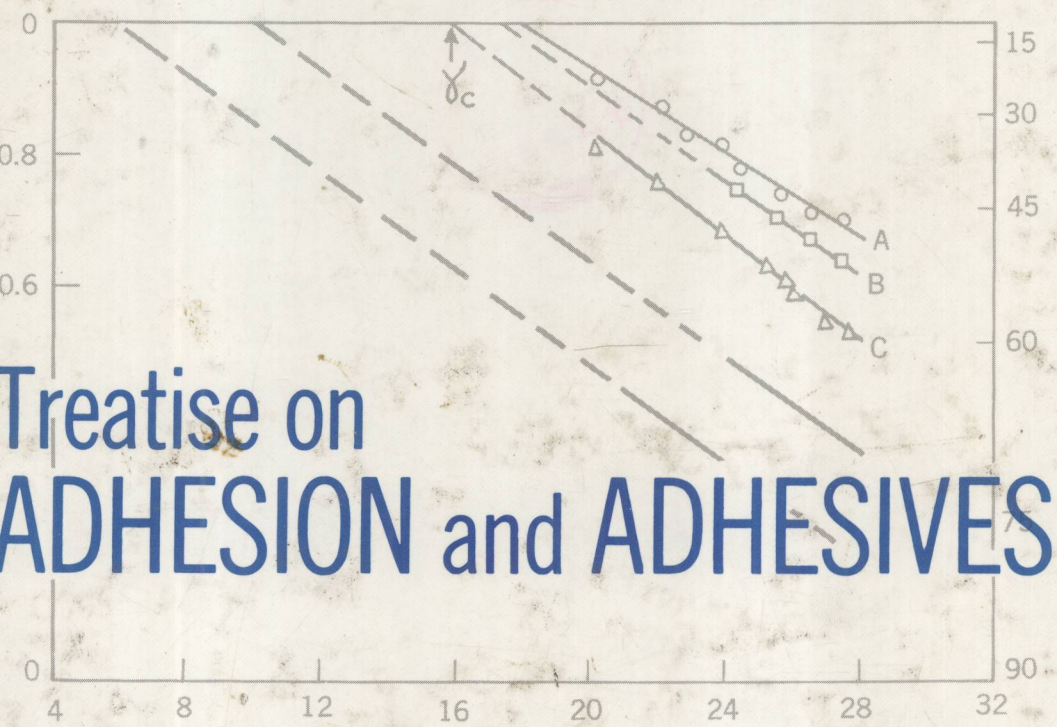


volume 5



Treatise on ADHESION and ADHESIVES

edited by
Robert L. Patrick

TREATISE ON ADHESION AND ADHESIVES

volume 5

edited by
Robert L. Patrick

MARCEL DEKKER, INC. New York and Basel

1021048

COPYRIGHT © 1981 by MARCEL DEKKER, INC.
ALL RIGHTS RESERVED

Neither this book nor any part may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopying, micro-filming, and recording, or by any information storage and retrieval system, without permission in writing from the publisher.

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

LIBRARY OF CONGRESS CATALOG CARD NUMBER: 66-11285
ISBN: 0-8247-1399-0

Current printing (last digit):
10 9 8 7 6 5 4 3 2 1

PRINTED IN THE UNITED STATES OF AMERICA

Preface

The *Treatise on Adhesion and Adhesives* was originally set at three volumes: the first volume to be theory, the second, technology, and the third, materials. As with all good intentions, the concept was carried out in the first case, was modified in the second case, and was substantially changed in the third. In addition, *Volume 4* provides a state-of-the-art review of structural adhesives in the form of a Materials Advisory Board report of the National Research Council of the National Academy of Sciences. Several respected colleagues debated the idea of including the MAB report; however, it would seem that the general public is often not aware of this type of document, and therefore some worthwhile reviews have been made available. Also, *Volume 4* provides a generalized roadmap for future work in the field.

Finally, *Volume 5* of the *Treatise* consists of a selection of special topics, starting with a critical review by J. R. Huntsberger of the relationships among interfacial energies, contact angle equilibria, and the work of adhesion. Since the early work of Zisman and coworkers, the contact angle has been used and misused by numberless workers in the field. In a concise treatment, Huntsberger points out the direct relation of the contact angle to estimating interfacial energies and the work of adhesion when solids are involved. The importance of a thorough understanding of fundamentals is stressed.

A new area of interest is covered in a chapter by Drzal concerning the advanced material, high modulus graphite. In the next few years, much will be heard concerning graphite fiber reinforced composites, and the requirement to understand and improve the graphite surface and surface interactions is paramount. The chapter reviews recent exciting work that was carried out by the author when examining the surface composition and surface energetics of graphite fibers derived from polyacrylonitrile. The third chapter is essentially a continuation of the work reported in *Volume 3* by J. Dean Minford. In an exhaustive treatment of durability studies carried out for as long as eight years,

the author points out the important interacting relationships of substrate composition, physical state, and geometry; the adhesion composition, as well as curing temperature; and the environmental considerations with and without stress. The chapter is essentially state-of-the-art as far as durability of bond with aluminum substrates is concerned. The next two chapters represent a monumental effort by Smith and Kaelble to examine the results of a detailed study of the effect of surface treatment on aluminum and titanium from a failure point of view. Using elegant techniques developed during the work, they have generated an outstanding contribution to the understanding of failure mechanisms.

Good has been concerned for several years about the semantics of adhesion; he offers a provocative discussion involving this subject. Lewis and Gounder have been considering the extension of the Prot equation to predict the performance and, therefore, the failure of adhesive joints. The approach is controversial and is included to stimulate thought and, hopefully, further experimentation in this area.

Volume 5 falls into the general category of special topics; however, it is obvious that the interface is preeminent in five of the seven chapters. This is not surprising inasmuch as there is considerable understanding of the substrates and the adhesives, respectively, while the interface is poorly understood. It is to be hoped that this volume will shed some additional light on this poorly illuminated area.

Robert L. Patrick

Contributors

Lawrence T. Drzal, Air Force Materials Laboratory, Wright Patterson
Air Force Base, Ohio

Robert J. Good, Department of Chemical Engineering, State University
of New York, Buffalo, New York

James R. Huntsberger, E. I. du Pont de Nemours & Company
Wilmington, Delaware

David H. Kaelble, Rockwell International, Thousand Oaks, California

Armand F. Lewis, Lord Corporation, Erie, Pennsylvania

J. Dean Minford, Alcoa Laboratories, Alcoa Center, Pennsylvania

R. Natarajan Gounder,* Lord Corporation, Erie, Pennsylvania

Tennyson Smith, Rockwell International, Thousand Oaks, California

*Present affiliation: RCA Laboratories, Princeton, New Jersey

Treatise on Adhesion and Adhesives

Contents of Other Volumes

editor
Robert L. Patrick

Volume 1: THEORY

Introduction, *Robert L. Patrick*

Intermolecular and Interatomic Forces, *Robert J. Good*

Adsorption of Polymers, *Robert R. Stromberg*

The Mechanisms of Adhesion, *J. R. Huntsberger*

Role of Bulk Properties of the Adhesive, *Turner Alfrey, Jr.*

Rheology of Polymers Used as Adhesives, *D. H. Kaelble*

Fracture Mechanics Applied to Adhesive Systems, *G. R. Irwin*

Variables and Interpretation of Some Destructive Cohesion and Adhesion Tests, *J. L. Gardon*

Surface Chemistry, *Frederick M. Fowkes*

Volume 2: MATERIALS

Introduction, *Robert L. Patrick*

Epoxide Adhesives, *Hans Dannenberg and Clayton A. May*

Thermosetting Adhesives, *Lawrence T. Eby*

Elastomeric Adhesives, *William C. Wake*

Pressure-sensitive Adhesives, *Carl A. Dahlquist*

Fiber Adhesion, *H. T. Patterson*

Soldering, Brazing, and Welding, *Floyd H. Bair*

Glass Resin Adhesion in Filament-wound Structures, *Samuel Brelant*

High-temperature Adhesion, *H. Levine*

Preparation of Ultraclean Substrate Surfaces, *V. Ponc*

Thermoplastic Adhesives, *Richard A. Weidener*

Volume 3

Structural Adhesives for Metal Bonding, *Justin C. Bolger*

Durability of Adhesive Bonded Aluminum Joints, *J. Dean Minford*

Adhesion and the Glassy State, *Gerald W. Miller*

The Use of Scanning Electron Microscopy, *R. L. Patrick*

Volume 4: STRUCTURAL ADHESIVES, with Emphasis on Aerospace Applications, *A Report of the ad hoc Committee on Structural Adhesives for Aerospace Use* National Materials Advisory Board, National Research Council

Introduction, Scope, Exclusions, Methodology

Summary of Conclusions and Recommendations

Current and Future Service Applications

Structural Adhesives Development

Interfacial Aspects of Structural Adhesive Bonding

Manufacturing and Processing

Behavior of Polymeric Adhesives in Joints

Design, Analysis, and Test Methods

Performance and Reliability

Technology Transfer and Utilization

**TREATISE ON
ADHESION AND ADHESIVES**
volume 5

Contents

Preface/ iii
Contributors/ v
Contents of Other Volumes/ ix

- 1 Interfacial Energies, Contact Angles, and Adhesion/ *James R. Huntsberger*/ 1
- 2 The Surface Composition and Energetics of Some PAN-Based Graphite Fibers/ *Lawrence T. Drzal*/ 21
- 3 Aluminum Adhesive Bond Permanence/ *J. Dean Minford*/ 45
- 4 Mechanisms of Adhesion Failure Between Polymers and Metallic Substrates: Aluminum 2024-T3 with HT424 Adhesive/ *Tennyson Smith and David H. Kaelble*/ 139
- 5 Mechanisms of Adhesion Failure Between Polymers and Metallic Substrates: Titanium 6Al-4V with HT424 Adhesive/ *Tennyson Smith and David H. Kaelble*/ 235
- 6 Semantic Physics of Adhesion/ *Robert J. Good*/ 293
- 7 Permanence and Endurance of Structural Adhesive Joints/ *Armand F. Lewis and R. Natarajan Gounder*/ 313

Author Index/ 383
Subject Index/ 391

Interfacial Energies, Contact Angles, and Adhesion

James R. Huntsberger

*E. I. du Pont de Nemours & Company
Wilmington, Delaware*

1. ATTRACTIVE FORCES AND ENERGIES

This chapter comprises a review of the relationships among interfacial energies, contact angle equilibria, and the reversible work of adhesion. The review is not intended to be comprehensive, but hopefully is sufficiently current and critical to be of some value.

Let us start by defining "adhesion" (as it will be used throughout this work) as the force or energy of attraction between two materials or phases which are in contact with each other. These attractive forces and energies are due mainly to dispersion and dipolar and induction interactions. In some cases hydrogen bonding or acid-base-type interactions may also be involved.

Various workers [1-6] have proposed models and calculated these forces using polarizabilities, electron vibrational frequencies, ionization potentials, and dipole moments as the source of attractive interactions. For the purpose of this review the important results are the apparent validity of the geometric mean as a means of calculating interactions between two materials and recognition that at interfacial separations less than 10 nm attractive forces are inversely proportional to the third power of the effective mean distance of intermolecular separation and attractive energies inversely proportional to the second power of the separation.

Another important result of these calculations is that they lead to a direct relationship between interfacial energies and the maximum attractive force or the reversible work of adhesion per unit area between phases. From Gardon [7]:

$$\sigma_{\max} = \frac{2.05\phi(\gamma_1\gamma_2)^{\frac{1}{2}}}{\bar{r}_{12}} \quad (1)$$

and from Good and Girifalco [1]:

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

In both of these equations ϕ is Good's interaction parameter, which corrects for any defects in the models used for calculation and for departures from ideality or regularity in interfacial interactions.

The parameter ϕ can be broken down into two factors: ϕ_a , which accounts for the departures from ideality in the intermolecular attractions; and ϕ_r , which accounts for departures from regularity in interfacial separations.

The importance of variations of ϕ_r has been dismissed frequently (e.g., Ref. 6) on the premise that only when differences between the average intermolecular separations of the phases is 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 and restrictions on conformations of polymer molecules at an interface make it highly probable that the effective mean interfacial separations will be 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 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 [8] 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 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 [9] showed that the low surface energies of fluoropolymers are mainly due 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 $\theta > 90^\circ$ increasing roughness increases advancing contact angles, but when $\theta < 90^\circ$ increasing roughness decreases advancing angles.

In the following discussion the interaction parameter ϕ will be considered as making the work of adhesion an exact thermodynamic value for a given pair of materials. However, whenever a value for ϕ is calculated rather than determined experimentally the value is an estimate of ϕ .

Estimates of ϕ_a can be obtained using equations of the form:

$$\phi_a = (d_1 d_2)^{\frac{1}{2}} + (p_1 p_2)^{\frac{1}{2}} + 0.0721 (d_2 p_1)^{\frac{1}{2}} + 0.0721 (d_1 p_2)^{\frac{1}{2}} + \Delta H + \Delta_{ab} \quad (3)$$

where d_i is the fraction of total interaction due to dispersion forces, p_i the fraction due to polar interactions, ΔH interactions due to hydrogen bonding, and Δ_{ab} acid-base interactions.

The third and fourth terms are due to induction [3].

At the present time inclusion of all of the terms in Eq. (3) is probably not warranted and the simplified equation

$$\phi_a = (d_1 d_2)^{\frac{1}{2}} + (p_1 p_2)^{\frac{1}{2}} \quad (4)$$

will be found useful and convenient.

Estimates for ϕ_r have been given [6] as:

$$\phi_r = \frac{r_{11} r_{12}}{[(r_{11} + r_{22})/2]^2} \quad (5)$$

but as discussed earlier are probably poor estimates of little value.

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

$$\gamma_{SL} = \gamma_{SO} + \gamma_{LV} - 2\phi(\gamma_{SO}\gamma_{LV})^{\frac{1}{2}} \quad (6)$$

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos \theta \quad (7)$$

$$\gamma_{SO} - \pi_e = \gamma_{SV} \quad (8)$$

$$\pi_{SL} - \pi_e = \gamma_{LV} \cos \theta \quad (9)$$

$$\pi_{SL} = \gamma_{SO} - \gamma_{SL} \quad (10)$$

$$\gamma_{SO} - \pi_e - \gamma_{SL} = \gamma_{LV} \quad \text{when } \theta = 0 \quad (11)$$

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 vapors. The equilibrium spreading pressure of the vapor on the solid is π_e , and π_{SL} is the equilibrium spreading pressure of the liquid on the solid.

Equation (11) is a statement of Anatoff's rule *at equilibrium*. This was shown [10] to be valid.

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

$$S_{2/13} = \gamma_{13} - \gamma_{12} - \gamma_{23} \quad (12)$$

$$= W_{adh}^{12} + W_{adh}^{23} - W_{adh}^{13} - 2\gamma_{2V} \quad (13)$$

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

For the special case where phase 3 is vapor:

$$S_{2/13} = W_{adh}^{12} - 2\gamma_{2V} \quad (14)$$

The following special values are obtained from the fundamental equations:

At $\theta = 0$; $S = 0$ (S = equilibrium spreading coeff.)

At $\theta = 90^\circ$; $\pi_{SL} = \pi_e$

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 Fig. 1-1. 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 Fig. 1-2. 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 [6].

The spreading pressure of the liquid on the solid π_{SL}/γ_{SO} is plotted in Fig. 1-3. The initial spreading coefficient S_i/γ_{SO} and the equilibrium spreading coefficient S/γ_{SO} are plotted in Figs. 1-4 and 1-5.

From Figs. 1-3 to 1-5 and equations (2), (6), (8), and (10) the following relationships are clear:

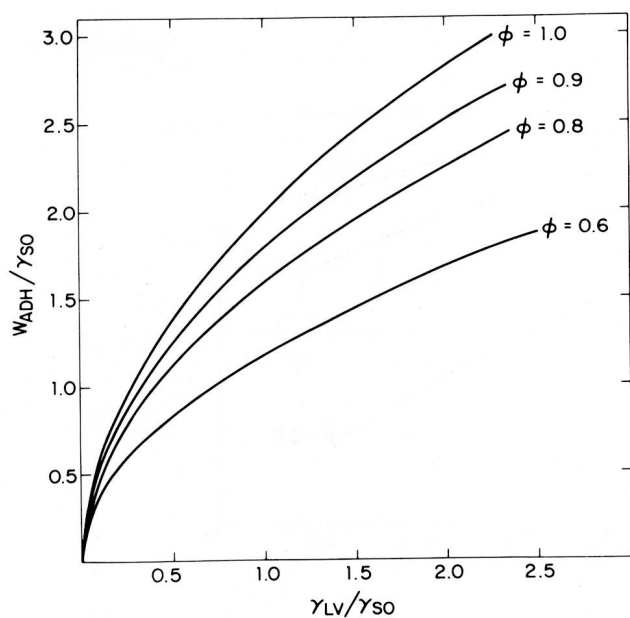


FIG. 1-1 Work of adhesion w_{ADH}/γ_{SO} vs. γ_{LV}/γ_{SO} for various values of ϕ .

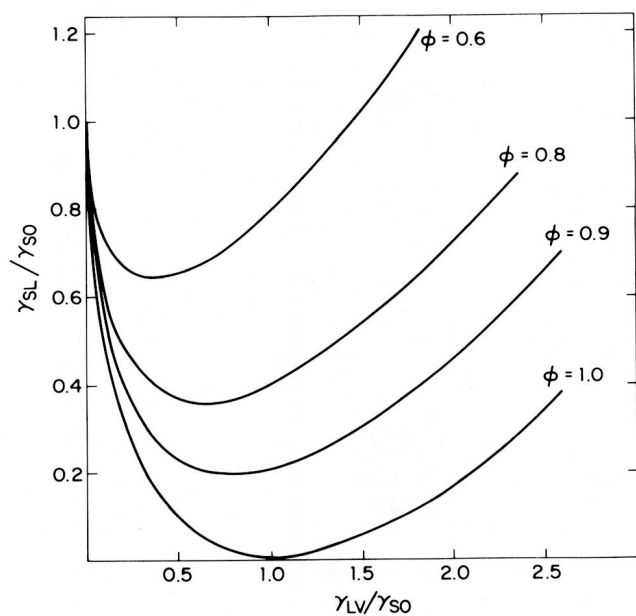


FIG. 1-2 Interfacial tension γ_{SL}/γ_{SO} vs. γ_{LV}/γ_{SO} for various values of ϕ .

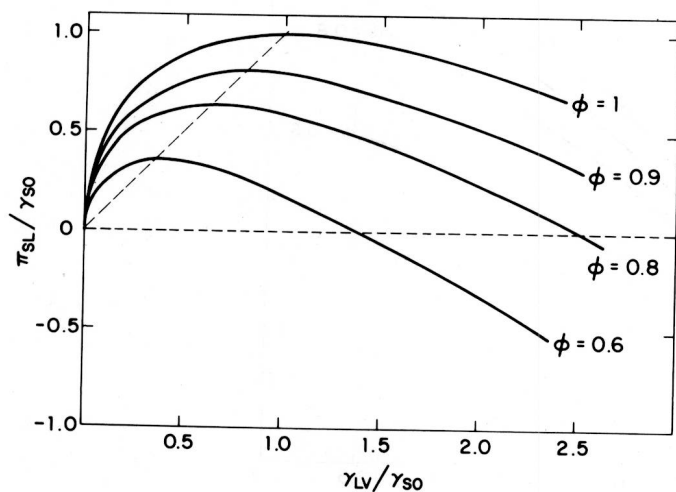


FIG. 1-3 Spreading pressure of liquid on the solid $(\pi_{SL})/\gamma_{SO}$ vs. γ_{LV}/γ_{SO} for various values of ϕ .

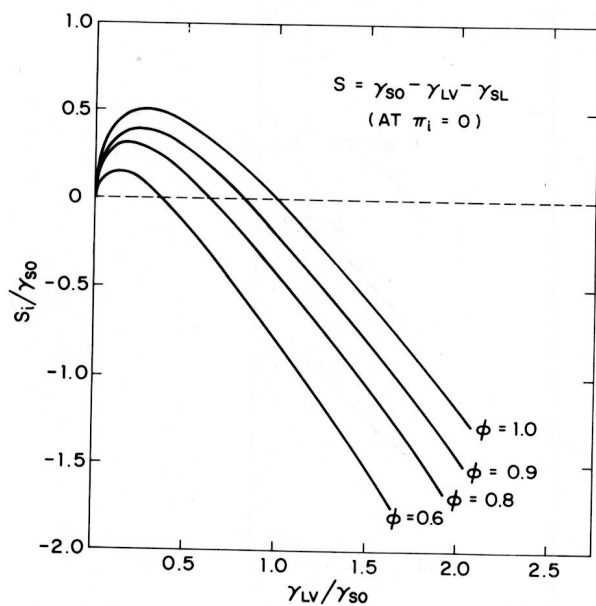


FIG. 1-4 Initial spreading coefficient S_i/γ_{SO} vs. γ_{LV}/γ_{SO} for various values of ϕ .

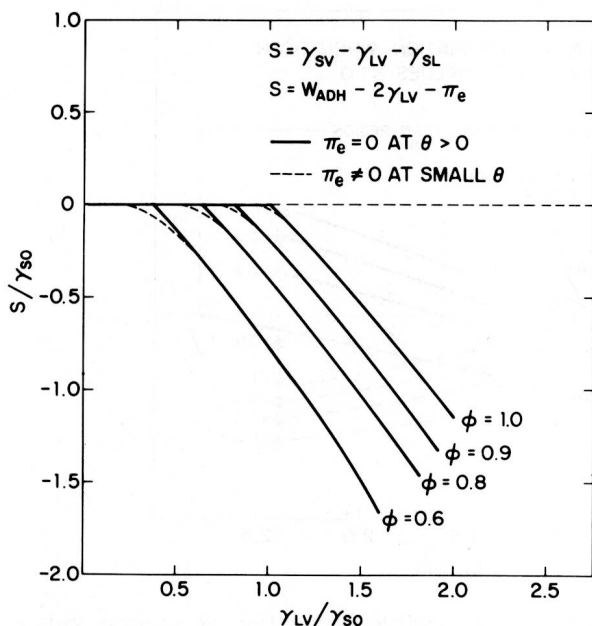


FIG. 1-5 Equilibrium spreading coefficient S/γ_{SO} vs. γ_{LV}/γ_{SO} for various values of ϕ .

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

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

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

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 $= 0.5\phi^2$.

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

In Fig. 1-7 $\cos \theta$ is plotted vs. the dimensionless γ_{LV}/γ_{SO} . These curves represent the theoretical basis for Zisman plots of $\cos \theta$ vs. γ_{LV} .