# THE THREE DIMENSIONAL SOLUBILITY PARAMETER AND SOLVENT DIFFUSION COEFFICIENT

## *Their Importance In Surface Coating Formulation*

*by*

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G. Hansen, C. M., "On the Application of the Three Dimensional Solubility Parameter to the Prediction of Mutual Solubility and Compatibility", Färg och Lack, **13,** No. 6, 132 (1967).

# Preface

The contents of this volume are based on more than four years of full-time research. During this time the author has been part of the staff of the Instituttet for Kemiindustri at the Technical University of Denmark, although the actual experimental work has been performed at the Danish Paint and Ink Research Laboratory (Lak- og Farveindustriens Forskningslaboratorium).

Much of the work in this volume has been published previously, giving it the character of a summary in many respects. More detail can be found in the original articles in these cases, though there is considerable original material included in this volume which has not been published previously. The references listed in this volume are intended as references only; the list is not a complete literature survey of the topics covered. This is in part due to the newness of much of the material, and in part due to its breadth, since it covers many fields. More references are to be found in the published articles.

The studies reported in this volume can not be considered finished. The solubility parameter studies are only a beginning for what the author hopes will eventually come. The immediate purpose of this volume is to stimulate interest in this approach to predicting interactions among materials, in the hope that others can carry on the work in their own special fields. The study of solvent retention has reached a stage where direct practical application is possible within the industries which deal with polymeric film formers.

Professor Anders Björkman, head of the Instituttet for Kemiindustri, has arranged for this study, has provided for the necessary financial support, and has given the author the freedom to pursue interesting problems as they appeared. Mr. H. K. Raaschou Nielsen, director of the Danish Paint and Ink Research Laboratory, has provided laboratory space, and initially suggested that a study in the area of solvent retention was lacking, thus starting the process leading to this volume. The author wishes to sincerely thank both Professor Anders Björkman and Mr. Raaschou Nielsen for their support and interest for his endeavors.

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The author would like to acknowledge the assistance of the staff at the Danish Paint and Ink Research Laboratory. Mr. Klemen Skaarup, in particular, has been

of great assistance in helping to develop the solubility parameter as a useful tool. We have, indeed, been co-authors, and independent publications by Mr. Skaarup can be expected in the future.

The author would also like to acknowledge the assistance rendered him from other institutions. The computer calculations have all been performed at the Northern Europe University Computing Center at no expense. The measurement of diffusion coefficients with radioisotopes was done at the Danish Isotope Center (Isotopcentralen) with the full co-operation of their staff, Mr. Bent Riber Petersen in particular.

Mr. Arne Vinther and Mr. Palle Sørensen at Køge Chemical Works have been particularly helpful in clarifying numerous situations dealing with pigments. Such interest and co-operation during the earlier stages of the study of pigment properties was timely and stimulating.

The author would also like to thank Mrs. G. Kastrup Olsen for typing most of his manuscripts.

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*Chapter 1*

# Introduction

This study is concerned with some new aspects of solvent properties, and how these properties can help predict paint behavior during the manufacturing and drying processes. These same solvent properties will be useful in predicting behavior in many other fields of endeavor; restriction of the conclusions reached in this study to the paint industry alone would seriously limit their usefulness. The work on the solubility parameter, in particular, deals with fundamental attractions among materials and should have broad application.

This study actually developed in the inverse order from that in which it is reported here. The author was first concerned with the question of film drying and solvent retention, the phenomenon that solvent can be found in many paint and varnish films years after their application. The usual assumption that hydrogen bonding is responsible for this retained solvent was shown to be false (A, B, C). Still further direct evidence supporting this conclusion has been included in the present volume.

To say that hydrogen bonding had no significant effect on solvent retention without defining hydrogen bonding was not satisfactory. In order to better define hydrogen bonding and polar bonding, a study based on the solubility parameter (Hildebrand and Scott 1949, 1962) was initiated. This study eventually led to the concept of a three dimensional solubility parameter (E), a concept which has been applied to the solution of many types of problems having importance in the paint and varnish industry. This new method of defining hydrogen and polar bonding did not alter the previous conclusions regarding solvent retention.

Rather than stop at saying hydrogen bonding did not significantly affect solvent retention, the reasons for solvent retention were explored experimentally and mathematically with good agreement between computer calculated drying curves based on the diffusion equation and drying curves measured in the laboratory. The reason for solvent retention is a low diffusion coefficient for the solvent in the polymer at low concentrations.

Diffusion coefficients for several solvents in poly(vinyl acetate) were found to be primarily dependent on molecular geometry. Since these diffusion coefficients vary up to six or seven decades in a narrow concentration interval, it was necessary to develop a new means of interpreting the experimental diffusion data. A procedure for this purpose was determined from new solutions to the diffusion equation.

The three dimensional solubility parameter concept turned out to be that portion of the study which has attracted the most interest. In addition to better defining hydrogen and polar bonding, it has been used to characterize solvents, plasticizers, polymers and resins, emulsifiers, numerous pigments, and dyes. Being able to characterize all these materials with the same parameter enabled interpretation of situations involving the solubilities of the various materials studied, mutual solubility and compatibility of polymers and resins, and certain phases of pigment dispersion. In view of these results all indications are that the three dimensional solubility parameter can help describe phenomena where there is a marked solvent effect, or where the materials involved can be characterized by their individual interactions with a series of solvents. Its use offers the possibility of a new concept in paint and printing ink formulation.

Suggestions for further work and numerous ideas for application of the solubility parameter in other areas such as surface chemistry are included in the last chapter.

## *Chapter 2*

# The Three Dimensional Solubility Parameter

### 2.1 *Introduction*

The original purpose of the work reported in this section was to better define the meaning of the terms hydrogen bonding, polar bonding, and polarity. Polymer solubility was studied to attempt this because it was polymer-solvent interactions which were of immediate interest. Polymer solubility also has the distinct advantage that it is a very large effect both to the eye and thermodynamically.

There have been numerous efforts to correlate polymer solubility. The usual approach has been to use the solubility parameter (Hildebrand and Scott 1949, 1962) in connection with some other parameter to account for hydrogen bonding. Burrell (1955, 1957, 1962) was the first to use the solubility parameter concept in more practical situations through a grouping of solvents according to their low, medium, or high hydrogen bonding capacities. Others (Lieberman 1962, Dyck 1964) have attempted to quantify a hydrogen bonding parameter, allowing two dimensional plotting of solubility regions on hydrogen bonding parameter versus solubility parameter diagrams. Crowley (Crowley et al. 1966) culminated this approach by introducing a three dimensional system with axes given by the solubility parameter, a hydrogen bonding parameter, and the dipole moment. The fundamental shortcoming in all these systems becomes obvious when one considers the definition of the solubility parameter. Since the solubility parameter contains all the energies holding the liquid together, the story lies within the solubility parameter itself. Each of these systems has been reasonably successful since it attempts to describe solubility in terms of factors which do relate directly to solubility, but fundamentally they must be considered strictly empirical.

The solubility parameter is defined as

$$\delta = (-e^o/V_m)^{\frac{1}{2}} \qquad (2.1)$$

where $-e^o$ is the molar potential energy of the liquid and $V_m$ is its molar volume. More theoretical aspects of the solubility parameter theory have been discussed in Danish by Sonnich Thompsen (1966A, B). For purposes of calculation this potential energy is replaced by the energy of evaporation of the solvent, $\Delta E$, and the solubility parameter is calculated as the square root of the cohesive energy density for all liquids whose vapors can be considered ideal.

2.2) $$\delta = (\text{c.e.d.})^{\frac{1}{2}} = \left[\frac{\Delta E}{V_m}\right]^{\frac{1}{2}} \quad \left[\frac{\text{cal}}{\text{cm}^3}\right]^{\frac{1}{2}}$$

$\Delta E$ includes the energies arising from all modes of interaction which hold the liquid together. The three major modes of interaction contributing to the cohesive energy density are dispersion (London) forces, polar forces, and hydrogen bonding. Since all these energies are included in the solubility parameter itself, the solubility parameter plus other parameters to account for these effects should not be necessary. This was in part realized by Blanks (1964) who divided the solubility parameter into dispersion and "polar" contributions by the homomorph concept. This approach provided the basis for the present study.

## 2.2 *The Three Dimensional Solubility Parameter*

It has been assumed that $\Delta E$ is given by the simple sum of the energies arising from dispersion forces, $\Delta E_d$, polar forces, $\Delta E_p$, and hydrogen bonding forces, $\Delta E_h$, according to Equation 2.3.

2.3) $$\Delta E = \Delta E_d + \Delta E_p + \Delta E_h$$

Equation 2.3 is the author's contribution to developing the solubility parameter as a more useful tool than it had been previously. Once this equation is written, the remainder of the story is logical and direct.

Dividing Equation 2.3 by the solvent molar volume yields

2.4) $$\frac{\Delta E}{V_m} = \frac{\Delta E_d}{V_m} + \frac{\Delta E_p}{V_m} + \frac{\Delta E_h}{V_m}$$

or

2.5) $$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2$$

The subscripted parameters defined as:

2.6) $$\delta_d = \left[\frac{\Delta E_d}{V_m}\right]^{\frac{1}{2}}$$

2.7) $$\delta_p = \left[\frac{\Delta E_p}{V_m}\right]^{\frac{1}{2}}$$

and

2.8) $$\delta_h = \left[\frac{\Delta E_h}{V_m}\right]^{\frac{1}{2}}$$

represent the effects of the dispersion forces, polar forces, and hydrogen bonding forces, respectively. According to Equation 2.5, the solubility parameter of a given solvent can be considered a vector with components $\delta_d$, $\delta_p$, and $\delta_h$. This means that each solvent can be located in a three dimensional system as a fixed point with co-ordinates agreeing with Equation 2.5. The axes of the system are the dispersion axis, $\bar{\delta}_d$, the polar axis $\bar{\delta}_p$, and the hydrogen bonding axis, $\bar{\delta}_h$. A sketch of this system is included in Figure 2.1.

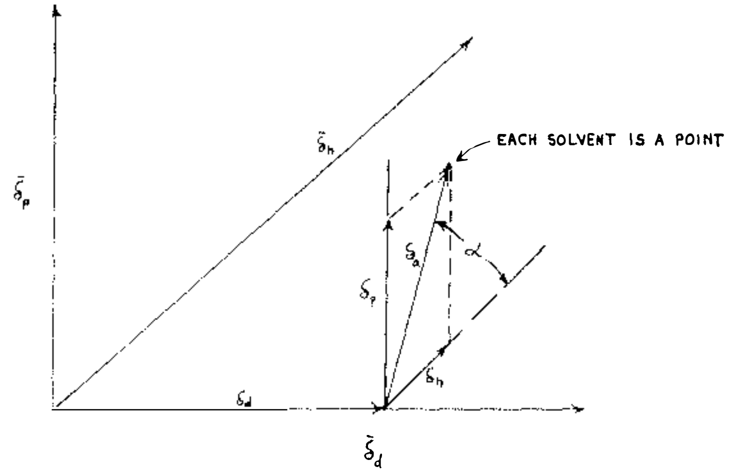


Figure 2.1. Sketch of the three dimensional system

## 2.3 *Thermodynamic Background*

The free energy of mixing for the solution process must be negative for solution to occur. This free energy, $\Delta G^M$, is given by

$$2.9)\qquad \Delta G^M = \Delta H^M - T\Delta S^M$$

where T is the absolute temperature and $\Delta H^M$ and $\Delta S^M$ are the enthalpy and entropy of mixing, respectively. Unless some very unusual form for order in the resulting mixture arises because of solvation (Moore and Shuttleworth 1963), the entropy term will be positive, and lead to a more negative $\Delta G^M$. In a given situation there is very little one can systematically do to improve solubility relations by considering the $T\Delta S$ term at the present time. This is not the case with the $\Delta H^M$ term (see also Chapter 8).

According to the Hildebrand solubility parameter theory, the energy of mixing, $\Delta E^M$, for two non-polar liquids is given by

$$2.10)\qquad \Delta E^M = \O_1\O_2\,(X_1V_{m1} + X_2V_{m2})\,(\delta_1 - \delta_2)^2$$

with the volume fractions being given by

2.11) $\phi_1 = X_1V_{m1}/(X_1V_{m1} + X_2V_{m2})$

2.12) $\phi_2 = X_2V_{m2}/(X_1V_{m1} + X_2V_{m2})$

and mole fractions given by

2.13) $X_1 = N_1/(N_1 + N_2)$

2.14) $X_2 = N_2/(N_1 + N_2)$

$N_1$ and $N_2$ are the number of molecules in the given liquid.

Since

2.15) $\Delta H^M = \Delta E^M + P\Delta V^M$

for a constant pressure process where P is the pressure and $\Delta V^M$ is the change of volume on mixing, and since the volume change on mixing is negligibly small for the systems considered, $\Delta H^M$ in Equation 2.9 can be replaced by $\Delta E^M$. Polymers are treated as liquids.

Considering Equation 2.10 it is obvious that at constant composition, $\Delta E^M$ will be low when the solubility parameters of the two liquids are close to each other. $\Delta E^M$ will also be smaller for liquids with low molar volumes.

There has not been any theory developed to include the effect of hydrogen bonding, although Blanks (1964) and later Gardon (1966) have worked with the effect of solvent polarities.

What was done in this study was to adopt the pragmatic procedure of "try and see what happens". It was assumed that the three dimensional solubility parameters of the solvent and the polymer must also be similar if $\Delta E^M$ is to be reduced. To support this assumption can be said, with hindsight, that the system has been unusually successful.

It is inherently assumed that any reaction in a given system will invalidate the theory. Where "compounds" are formed, such as dimethyl sulphoxide:$2H_2O$ (Lindenfors 1967) special considerations have to be made, though the system consisting of carbon tetrachloride-benzene(1:1) did not show any obvious deviations in the solubility of the solutes studied (Goates et al. 1959).

## 2.4 *Placing the Solvents*

The initial approach to the division of the solubility parameter, $\delta$, into components representing dispersion, polar, and hydrogen bonding forces was based on the homomorph concept and trial and error placements of the solvents as points in a three dimensional system (E). $\Delta E_d$ was calculated directly as the energy of evaporation of the homomorph, or hydrocarbon counterpart, of an active solvent by the method described by Blanks (1964). The homomorph should have the same size and shape as the solvent in question, with the evaluation of $\Delta E_d$ being made at the temperature corresponding to the reduced temperature of the solvent. This is, unfortunately, not always possible. Knowing $\Delta E_d$ allowed calculations of $\delta_d$ from Equation 2.6.

Estimation of the effect of the active portion of the solvent molecule was made by subtracting $\Delta E_d$ from $\Delta E$. This quantity was called the association energy, $\Delta E_a$. Thus,

2.16) $$\Delta E_a = \Delta E - \Delta E_d = \Delta E_p + \Delta E_h$$

Dividing Equation 2.16 by $V_m$ yields

2.17) $$\delta_a^2 = \delta_p^2 + \delta_h^2$$

where

2.18) $$\delta_a = \left[\frac{\Delta E_a}{V_m}\right]^{\frac{1}{2}}$$

Equation 2.17 says that $\delta_a$ is the vector sum of $\delta_p$ and $\delta_h$. What was known then was $\delta_d$ and the vector sum of $\delta_p$ and $\delta_h$. Solvents were located in the system as points by trial and error in accordance with these requirements. It was possible to arrange the placement of about 90 solvents (listed in Table 2.1) such that all those solvents dissolving a given polymer or resin were located as points which clustered together. The 33 polymers and resins listed in Table 2.2 were treated in this manner. Requiring closed volumes of solubility for each solute is the equivalent of requiring the similarity of the three dimensional solubility parameters of the solute and the solvents which dissolve it.

The homomorph approach failed in the case of solvents containing chlorine or sulfur atoms. It was also obvious that proper cyclic homomorphs were particularly hard to choose.

## 2.5 *Revised Placements of the Solvents*

The initial trial and error placements of the solvents were revised when correlations with hydrogen bonding tendencies of the alcohols and polar bonding tendencies of numerous of the solvents were found (F). The revised placements given in Table 2.1 as $\delta_d$, $\delta_p$, and $\delta_h$ deviate significantly from the original trial and error placements in only few cases. They are in very good agreement with all solubility data taken to date. Typical plots of solubility data are included in Chapter 4. $\delta_P$ and $\delta_H$ are calculated as described in Sections 2.6 and 2.7 and are included for comparison in Table 2.1.

Table 2.1
Revised and Calculated Components of the Solubility Parameter

| | Revised | | | | | Calculated | |
|---|---|---|---|---|---|---|---|
| | δ | $\delta_d$ | $\delta_p$ | $\delta_h$ | $\delta_a$ | $\delta_P$ | $\delta_H$ |
| 1 Methanol | 14.28 | 7.42 | 6.0 | 10.9 | 12.40 | 6.2 | 11.0 |
| 3 Ethanol 99.9% | 12.92 | 7.73 | 4.3 | 9.5 | 10.45 | 4.3 | 9.3 |
| 4 n-Propanol | 11.97 | 7.75 | 3.3 | 8.5 | 9.10 | 3.2 | 8.2 |
| 5 n-Butanol | 11.30 | 7.81 | 2.8 | 7.7 | 8.20 | 2.7 | 7.4 |
| 6 Pentanol-1 | 10.61 | 7.81 | 2.2 | 6.8 | 7.17 | 2.2 | 6.8 |
| 7 2-Ethyl butanol | 10.38 | 7.70 | 2.1 | 6.6 | 6.94 | – | 6.4 |
| 8 2-Ethyl hexanol | 9.85 | 7.78 | 1.6 | 5.8 | 6.03 | – | 5.6 |
| 9 Methyl isobutyl carbinol | 9.72 | 7.47 | 1.6 | 6.0 | 6.22 | – | 6.3 |
| 10 Propylene glycol | 14.80 | 8.24 | 4.6 | 11.4 | 12.28 | 4.6 | 11.7 |
| 11 Ethylene glycol | 16.30 | 8.25 | 5.4 | 12.7 | 14.02 | 6.2 | 13.4 |
| 12 1,3 Butanediol | 14.14 | 8.10 | 4.9 | 10.5 | 11.60 | – | 10.5 |
| 13 Glycerol | 21.1 | 8.46 | – | – | 19.31 | 5.9 | 14.3 |
| 14 Cyclohexanol | 10.95 | 8.50 | 2.0 | 6.6 | 6.93 | 2.4 | 6.9 |
| 15 m-Cresol | 11.11 | 8.82 | 2.5 | 6.3 | 6.77 | 2.2 | 6.9 |
| 15A Ethyl lactate | – | 7.80 | 3.7 | 6.1 | 7.13 | – | 6.6 |
| 15B n-Butyl lactate | – | 7.65 | 3.2 | 5.0 | 5.94 | – | 5.8 |
| 16 Diethylene glycol | 14.60 | 7.86 | 7.2 | 10.0 | 12.29 | – | 10.2 |
| 17 Dipropylene glycol* | 15.52 | 7.77 | 9.9 | 9.0 | 13.35 | – | 8.7 |
| 18 2-Butoxyethanol | 10.25 | 7.76 | 3.1 | 5.9 | 6.67 | – | 6.2 |
| 19 Methyl dioxitol | 10.72 | 7.90 | 3.8 | 6.2 | 7.26 | – | 6.5 |
| 19A Butyl dioxitol | 8.96 | 7.80 | 3.4 | 5.2 | 6.23 | – | 5.4 |
| 20 Oxitol (Cellosolve) | 11.88 | 7.85 | 4.5 | 7.0 | 8.55 | – | 7.2 |
| 21 Diacetone alcohol | 10.18 | 7.65 | 4.0 | 5.3 | 6.60 | – | 6.3 |
| 22 Cellosolve acetate | 9.60 | 7.78 | 2.3 | 5.2 | 5.63 | 2.3 | – |
| 22A Methyl Cellosolve | 12.06 | 7.90 | 4.5 | 8.0 | 8.30 | – | 8.0 |
| 23 Diethyl ether | 7.62 | 7.05 | 1.4 | 2.5 | 2.88 | 1.4 | |
| 23A Furan | 9.09 | 8.70 | 0.9 | 2.6 | 2.70 | 0.9 | |
| 24 Dioxane* | 10.00 | 9.30 | 0.9 | 3.6 | 3.71 | 0.4 | |
| 25 Methylal* | 8.52 | 7.35 | 0.9 | 4.2 | 4.32 | 0.4 | |
| 26 Diethyl sulfide | 8.46 | 8.25 | 1.5 | 1.0 | 1.81 | 1.5 | |
| 26A Carbon disulfide | 9.97 | 9.97 | 0 | 0 | 0 | 0 | – |
| 26B Dimethyl sulphoxide | 12.93 | 9.00 | 8.0 | 5.0 | 9.43 | 8.7 | – |
| 27 Propylene carbonate | 13.30 | 9.83 | 8.8 | 2.0 | 9.00 | – | – |
| 28 γ-Butyrolactone | 12.78 | 9.26 | 8.1 | 3.6 | 8.82 | – | – |
| 29 Acetone | 9.77 | 7.58 | 5.1 | 3.4 | 6.13 | 5.1 | |
| 30 Methyl ethyl ketone | 9.27 | 7.77 | 4.4 | 2.5 | 5.06 | 4.5 | – |
| 31 Methyl isobutyl ketone | 8.57 | 7.49 | 3.0 | 2.0 | 4.15 | 3.2 | – |
| 31A Methyl isoamyl ketone | 8.55 | 7.80 | 2.8 | 2.0 | 3.44 | – | – |
| 32 Diisobutyl ketone | 8.17 | 7.77 | 1.8 | 2.0 | 2.64 | | |
| 32A Isophorone | 9.71 | 8.10 | 4.0 | 3.6 | 5.37 | | |
| 32B Acetophenone | 9.68 | 8.55 | 4.2 | 1.8 | 4.59 | 4.0 | – |
| 33 Cyclohexanone | 9.88 | 8.65 | 4.1 | 2.5 | 4.79 | 4.6 | – |
| 33A Tetrahydrofuran | 9.52 | 8.22 | 2.8 | 3.9 | 4.78 | 2.6 | – |
| 34 Mesityl oxide | 9.20 | 7.97 | 3.5 | 3.0 | 4.59 | 3.7 | – |
| 35 Ethyl acetate | 9.10 | 7.44 | 2.6 | 4.5 | 5.19 | 2.6 | – |

Table 2.1 (continued)

| | Revised | | | | | Calculated | |
|---|---|---|---|---|---|---|---|
| | $\delta$ | $\delta_d$ | $\delta_p$ | $\delta_h$ | $\delta_a$ | $\delta_P$ | $\delta_H$ |
| 36 n-Butyl acetate.......... | 8.46 | 7.67 | 1.8 | 3.1 | 3.58 | 1.8 | – |
| 36A Isoamyl acetate......... | 8.32 | 7.45 | 1.5 | 3.4 | 3.73 | 1.6 | – |
| 37 Isobutyl isobutyrate..... | 8.04 | 7.38 | 1.4 | 2.9 | 3.22 | – | – |
| 38 Acetonitrile............. | 11.9 | 7.50 | 8.8 | 3.0 | 9.30 | 9.6 | – |
| 38A Butyronitrile............ | 9.96 | 7.50 | 6.1 | 2.5 | 6.60 | 6.3 | – |
| 39 Nitromethane........... | 12.30 | 7.70 | 9.2 | 2.5 | 9.53 | 9.6 | – |
| 40 Nitroethane............ | 11.09 | 7.80 | 7.6 | 2.2 | 7.91 | 7.3 | – |
| 41 2-Nitropropane......... | 10.02 | 7.90 | 5.9 | 2.0 | 6.23 | 6.4 | – |
| 42 Aniline................ | 11.04 | 9.53 | 2.5 | 5.0 | 5.59 | 2.4 | – |
| 43 Nitrobenzene........... | 10.62 | 8.60 | 6.0 | 2.0 | 6.32 | 6.4 | – |
| 44 Ethanolamine........... | 15.48 | 8.35 | 7.6 | 10.4 | 12.90 | 7.4 | – |
| 45 Dimethyl formamide..... | 12.14 | 8.52 | 6.7 | 5.5 | 8.69 | – | – |
| 46 Dipropyl amine......... | 7.79 | 7.50 | 0.7 | 2.0 | 2.13 | – | – |
| 47 Diethyl amine........... | 7.96 | 7.30 | 1.1 | 3.0 | 3 18 | 1.1 | – |
| 47A Morpholine............ | 10.52 | 9.20 | 2.4 | 4.5 | 5.10 | 2.5 | – |
| 47B Cyclohexylamine........ | 9.05 | 8.45 | 1.5 | 3.2 | 3.53 | 1.5 | – |
| 47C Pyridine................ | 10.61 | 9.25 | 4.3 | 2.9 | 5.18 | 4.3 | – |
| 48 Carbon tetrachloride..... | 8.65 | 8.65 | 0 | 0 | 0 | 0 | – |
| 49 Chloroform............ | 9.21 | 8.65 | 1.5 | 2.8 | 3.20 | 1.8 | – |
| 50 Ethylene chloride........ | 9.76 | 9.20 | 2.6 | 2.0 | 3.28 | 2.6 | – |
| 51 Methylene chloride...... | 9.93 | 8.91 | 3.1 | 3.0 | 4.31 | 3.1 | – |
| 52 1,1,1 Trichloroethane.... | 8.57 | 8.25 | 2.1 | 1.0 | 2.33 | 2.2 | – |
| 52A 1-Chlorobutane.......... | 8.46 | 7.95 | 2.7 | 1.0 | 2.88 | 2.7 | – |
| 53 Trichloroethylene....... | 9.28 | 8.78 | 1.5 | 2.6 | 3.01 | 1.3 | – |
| 53A 2,2Dichloro diethyl ether* | 10.33 | 9.20 | 4.4 | 1.5 | 4.65 | 3.4 | – |
| 54 Chlorobenzene.......... | 9.57 | 9.28 | 2.1 | 1.0 | 2.33 | 2.1 | – |
| 55 o-Dichlorobenzene...... | 9.98 | 9.35 | 3.1 | 1.6 | 3.49 | 3.1 | – |
| 56 α-Bromonaphthaline..... | 10.25 | 9.94 | 1.5 | 2.0 | 2.50 | 1.5 | – |
| 56A Cyclohexylchloride...... | 8.99 | 8.50 | 2.7 | 1.0 | 2.88 | 2.7 | – |
| 57 Benzene................ | 9.15 | 8.95 | 0.5 | 1.0 | 1.11 | 0 | – |
| 58 Toluene................ | 8.91 | 8.82 | 0.7 | 1.0 | 1.22 | 0.4 | – |
| 59A Xylene................. | 8.80 | 8.65 | 0.5 | 1.5 | 1.58 | 0.5 | – |
| 59 Ethyl benzene.......... | 8.80 | 8.70 | 0.3 | 0.7 | 0.76 | 0.3 | – |
| 60 Styrene................ | 9.30 | 9.07 | 0.5 | 2.0 | 2.06 | 0.3 | – |
| 61 Tetralin................ | 9.50 | 9.35 | 1.0 | 1.4 | 1.72 | 1.0 | – |
| 62 Hexane................ | 7.24 | 7.24 | 0 | 0 | 0 | 0 | – |
| 63 Cyclohexane........... | 8.18 | 8.18 | 0 | 0 | 0 | 0 | – |
| 64 Water*................ | 23.5 | 6.0 | 15.3 | 16.7 | 22.8 | 15.3 | 16.7 |
| 65 Acetic acid*............ | 10.50 | 7.10 | 3.9 | 6.6 | 8.29 | 3.9 | – |
| 66 Formic acid* (90%)..... | 12.15 | 7.0 | 5.8 | 8.1 | 9.96 | – | |
| 67A Butyric acid*........... | – | 7.30 | 2.0 | 5.2 | 5.57 | 2.0 | – |
| 68 Benzaldehyde........... | 10.40 | 9.15 | 4.2 | 2.6 | 4.94 | 4.2 | – |
| 69 Acetic anhydride*....... | 10.30 | 7.50 | 5.4 | 4.7 | 7.16 | 4.4 | – |

* Relatively uncertain

Table 2.2
List of Polymers and Resins Studied

| | |
|---|---|
| A | Lucite® 2042-poly (ethyl methacrylate), E. I. du Pont de Nemours & Co., Inc. |
| B | Poly (methyl methacrylate), Rohm and Haas Co. |
| C | Epikote® 1001-epoxy, Shell Chemical Co. |
| D | Plexal P65-66% oil length alkyd, Polyplex. |
| E | Pentalyn® 830-alcohol soluble rosin resin, Hercules Incorported. |
| F | Butvar® B76-poly (vinyl butyral), Shawinigan Resins Co. |
| G | Polystyrene LG, Badische Anilin- und Soda Fabrik. |
| H | Mowilith® 50-poly (vinyl acetate), Farbwerke Hoechst. |
| I | Plastopal H-urea formaldehyde resin, Badische Anilin- und Soda Fabrik. |
| J | ½ Sec. Nitrocellulose-H 23, A. Hagedorn and Co., Osnabrück, W. Germany. |
| K | Parlon® P10-chlorinated poly (propylene), Hercules Incorporated. |
| L | Cellulose acetate, Cellidora A-Bayer AG. |
| M | Super Beckacite® 1001-Pure Phenolic Resin, Reichhold Chemicals Co.—Hamburg. |
| N | Phenodur 373U-phenol-resol resin, Chemische Werke Albert-Wiesbaden. |
| O | Cellolyn 102-modified pentaerythritol ester of rosin, Hercules Incorporated. |
| P | Pentalyn 255-alcohol soluble resin, Hercules Incorporated. |
| Q | Suprasec F5100-blocked isocyanate (phenol), Imperial Chemical Ind. Ltd. |
| R | Plexal C34-34% coconut oil-phthalic anhydride alkyd, Polyplex. |
| S | Desmophen 850, Polyester-Farbenfabriken Bayer AG. Leverkusen. |
| T | Polysar 5630—styrene-butadiene (SBR) raw elastomer, Polymer Corp. |
| U | Hycar® 1052-acrylonitrile-butadiene raw elastomer, B. F. Goodrich Chemical Corp. |
| V | Cariflex IR 305-isoprene raw elastomer, Shell Chemical Co. |
| X | Lutonal IC/123-poly (isobutylene), Badische Anilin- und Soda Fabrik. |
| Y | Buna Huls CB 10-cis poly butadiene raw elastomer, Chemische Werke Huels. |
| Z | Versamid® 930-polyamide, General Mills, Inc. |
| Ā | Ester gum BL, Hercules Incorporated. |
| B̄ | Cymel® 300-hexamethoxy melamine, American Cyanamid Co. |
| C̄ | Piccolyte® S100-terpene resin, Pennsylvania Industrial Chemical Corp. |
| D̄ | Durez® 14383-furfuryl alcohol resin, Hooker Chemical Co. |
| Ē | Piccopale® 110-petroleum hydrocarbon resin, Pennsylvania Industrial Chemical Corp. |
| F̄ | Vipla KR-poly (vinyl chloride), K=50, Montecatini. |
| Ḡ | Piccoumarone 450L-cumarone-indene resin, Pennsylvania Industrial Chemical Corp. |
| L̄ | Milled wood lignin—Special sample from prof. A. Björkman (Björkman 1956). |

The solubility data listed in Table 2.3 have been judged on a scale from 1 to 6 according to:

1 Soluble
2 Almost soluble
3 Strongly swollen, slight solubility
4 Swollen
5 Slight effect
6 No visible effect

The solutes are listed in Table 2.2; their solubility parameters are included in Table 4.1.

For nitriles, nitro compounds, and organic acids, the new values represent a compromise between the homomorph concept and the correlations given below. The $\delta_d$ values calculated from the homomorph comparison have been decreased to increase $\delta_a$. It may well be that $\delta_h$ should be increased more for formic acid and acetic acid, in which case $\delta_d$ would be decreased still more. As the linear hydrocarbon portion of a homologous series of solvents increases, the values should tend to converge at a value close to 8.1 on the $\delta_d$ axis, the solubility parameter of polyethylene. The placements of the aromatic hydrocarbons are rather arbitrary, since their homomorphs are very difficult to choose and no accurate $\delta_a$ values can be calculated for them (E). The placement of water must be considered very uncertain.

A number of low molecular weight plasticizers have been included in the system as points. This was done on the basis of their solubility relations with the same 33 polymers and resins. If they dissolved a number of the solutes, they must be included within the volumes of solubility for each. This allowed an approximate placement since the plasticizer must then be located in the region of overlap included in the solubility volumes of each of the solutes it dissolved. These placements are included in Table 2.4. Plasticizers could have been determined as volumes, just as solvents will also have volumes of miscibility but, in general, point placements are to be preferred. The miscibility volumes are very large for solvents and low molecular weight plasticizers.

The placements of both solvents and plasticizers have been checked by testing the solubility of the solutes in mixtures of non-solvents. If one non-solvent for a given solute located on one side of its volume of solubility is mixed with another non-solvent located on the opposite side, the resulting mixture should, according to the initial assumption, dissolve the solute. This has always been found to be the case, with the exception of a very few boundary region cases. Numerous such solvent combinations which dissolve the various solutes have been reported (E), and many more can be found quite simply by plotting the solubility data for the respective materials.

## 2.6 *Correlation with Hydrogen Bonding*

Infrared spectroscopy and other measurements indicate a reasonable value for the OH...O bond is 5000 calories/mole (Pimentel 1960). If one ascribes 5000 cal. of the energy of evaporation of a solvent to the presence of each alcohol group it contains, one can estimate the cohesive energy density and corresponding hydrogen bonding solubility parameter for the solvent.

Table 2.3—Solubility Data for

| | | A | B | C | D | E | F | G | H | I | J | K | L | M | N | O |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Methanol | 5 | 6 | 4 | 5 | 4 | 5 | 6 | 1 | 3 | 1 | 6 | 6 | 2 | 1 | 4 |
| 2 | Ethanol 96% | 4 | 6 | 4 | 6 | 4 | 1 | 6 | 1 | 1 | 6 | 6 | 6 | 1 | 1 | 5 |
| 3 | Ethanol 99.9% | 5 | 6 | 3 | 5 | 1 | 1 | 6 | 4 | 1 | 3 | 6 | 6 | 1 | 1 | 5 |
| 4 | n-Propanol | 5 | 6 | 3 | 5 | 1 | 1 | 6 | 4 | 1 | 6 | 6 | 6 | 1 | 1 | 2 |
| 5 | n-Butanol | 5 | 6 | 3 | 5 | 1 | 1 | 6 | 5 | 1 | 6 | 6 | 6 | 1 | 1 | 1 |
| 6 | Pentanol-l | 4 | 6 | 5 | 3 | 1 | 1 | 6 | 2 | 1 | 6 | 6 | 6 | 1 | 1 | 1 |
| 7 | 2-Ethyl butanol | 3 | 2 | 5 | 1 | 1 | 1 | 6 | 5 | 1 | 6 | 6 | 6 | 1 | 6 | 1 |
| 8 | 2-Ethyl hexanol | 4 | 2 | 5 | 1 | 1 | 1 | 6 | 5 | 1 | 6 | 6 | 6 | 1 | 6 | 1 |
| 9 | Methyl isobutyl carbinol | 4 | 5 | 5 | 1 | 1 | 1 | 6 | 5 | 1 | 6 | 6 | 6 | 1 | 6 | 1 |
| 10 | Propylene glycol | 6 | 6 | 5 | 6 | 4 | 6 | 6 | 6 | 1 | 6 | 6 | 6 | 6 | 1 | 6 |
| 11 | Ethylene glycol | 6 | 6 | 6 | 4 | 6 | 6 | 6 | 6 | 6 | 6 | 6 | 6 | 6 | 1 | 6 |
| 12 | 1,3 Butanediol | 5 | 6 | 5 | 5 | 4 | 6 | 6 | 6 | 5 | 6 | 6 | 6 | 6 | 1 | 6 |
| 13 | Glycerol | 4 | 6 | 6 | 5 | 6 | 6 | 6 | 6 | 6 | 6 | 6 | 6 | 6 | 6 | 6 |
| 14 | Cyclohexanol | 5 | 6 | 1 | 1 | 1 | 1 | 6 | 1 | 1 | 6 | 6 | 3 | 1 | 1 | 1 |
| 15 | m-Cresol | 3 | 3 | 1 | 1 | 1 | 1 | 5 | 1 | 1 | 5 | 6 | 4 | 1 | 1 | 1 |
| 15A | Ethyl lactate | 1 | 1 | 1 | 1 | 1 | 1 | 6 | 1 | 1 | 1 | 5 | 1 | 1 | 1 | 1 |
| 15B | n-Butyl lactate | 1 | 1 | 1 | 1 | 1 | 1 | 5 | 1 | 1 | 1 | 1 | 6 | 1 | 1 | 1 |
| 16 | Diethylene glycol | 6 | 6 | 1 | 5 | 3 | 5 | 6 | 6 | 4 | 1 | 6 | 6 | 4 | 1 | 6 |
| 17 | Dipropylene glycol | 6 | 6 | 1 | 6 | 1 | 5 | 6 | 5 | 1 | 1 | 6 | 6 | 1 | 1 | 5 |
| 18 | 2-Butoxyethanol | 1 | 5 | 1 | 1 | 1 | 1 | 6 | 2 | 1 | 1 | 2 | 6 | 1 | 1 | 1 |
| 19 | Methyl dioxitol | 1 | 1 | 1 | 1 | 1 | 1 | 6 | 1 | 1 | 1 | 4 | 4 | 1 | 1 | 1 |
| 19A | Butyl dioxitol | 1 | 3 | 1 | 1 | 1 | 1 | 4 | 1 | 1 | 1 | 1 | 6 | 1 | 1 | 1 |
| 20 | Oxitol (Cellosolve) | 1 | 5 | 1 | 1 | 1 | 1 | 5 | 1 | 1 | 1 | 5 | 6 | 1 | 1 | 1 |
| 21 | Diacetone alcohol | 1 | 2 | 1 | 1 | 1 | 1 | 5 | 1 | 1 | 1 | 3 | 4 | 1 | 1 | 1 |
| 22 | Cellosolve acetate | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 5 | 1 | 1 | 4 | 1 | 1 | 1 |
| 22A | Methyl Cellosolve | 4 | 3 | 1 | 1 | 1 | 1 | 6 | 1 | 1 | 1 | 6 | 4 | 1 | 1 | 2 |
| 23 | Diethyl ether | 3 | 6 | 3 | 1 | 4 | 5 | 3 | 4 | 6 | 6 | 6 | 6 | 1 | 5 | 1 |
| 23A | Furan | 1 | 4 | 1 | 1 | 1 | 1 | 1 | 1 | 3 | 6 | 3 | 6 | 1 | 6 | 1 |
| 24 | Dioxane | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 6 | 6 | 1 | 1 | 1 | 1 | 1 |
| 25 | Methylal | 1 | 5 | 1 | 1 | 1 | 1 | 1 | 1 | 6 | 1 | 5 | 5 | 1 | 3 | 1 |
| 26 | Diethyl sulfide | 1 | 4 | 4 | 1 | 1 | 5 | 1 | 3 | 5 | 6 | 1 | 6 | 1 | 6 | 1 |
| 26A | Carbon disulfide | 4 | 5 | 3 | 1 | 5 | 5 | 1 | 4 | 5 | 6 | 1 | 6 | 1 | 6 | 1 |
| 26B | Dimethyl sulphoxide | 4 | 1 | 1 | 3 | 1 | 2 | 6 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 4 |
| 27 | Propylene carbonate | 1 | 1 | 1 | 5 | 6 | 6 | 6 | 1 | 6 | 1 | 6 | 3 | 1 | 1 | 6 |
| 28 | γ-Butyrolactone | 1 | 1 | 1 | 6 | 1 | 3 | 1 | 1 | 1 | 1 | 3 | 1 | 1 | 1 | 5 |
| 29 | Acetone | 1 | 1 | 1 | 1 | 1 | 1 | 3 | 1 | 6 | 1 | 3 | 1 | 1 | 1 | 3 |
| 30 | Methyl ethyl ketone | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 6 | 1 | 1 | 4 | 1 | 1 | 1 |
| 31 | Methyl isobutyl ketone | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 6 | 1 | 1 | 6 | 1 | 1 | 1 |
| 31A | Methyl isoamyl ketone | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 6 | 1 | 1 | 6 | 1 | 1 | 1 |
| 32 | Diisobutyl ketone | 1 | 3 | 4 | 1 | 1 | 5 | 3 | 5 | 6 | 1 | 1 | 6 | 1 | 6 | 1 |
| 32A | Isophorone | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 6 | 1 | 1 | 1 |
| 32B | Acetophenone | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| 33 | Cyclohexanone | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 3 | 1 | 1 | 1 |
| 33A | Tetrahydrofuran | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| 34 | Mesityl oxide | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 5 | 1 | 1 | 6 | 1 | 1 | 1 |
| 35 | Ethyl acetate | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 6 | 1 | 1 | 5 | 1 | 1 | 1 |
| 36 | n-Butyl acetate | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 6 | 1 | 1 | 6 | 1 | 6 | 1 |
| 36A | Isoamyl acetate | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 5 | 1 | 1 | 6 | 1 | 6 | 1 |
| 37 | Isobutyl isobutyrate | 1 | 5 | 5 | 1 | 5 | 5 | 1 | 5 | 5 | 1 | 1 | 6 | 1 | 6 | 1 |
| 38 | Acetonitrile | 1 | 6 | 1 | 6 | 5 | 5 | 4 | 1 | 6 | 1 | 6 | 4 | 1 | 5 | 5 |
| 38A | Butyronitrile | 1 | 1 | 1 | 1 | 3 | 2 | 1 | 1 | 5 | 1 | 3 | 4 | 1 | 3 | 3 |
| 39 | Nitromethane | 1 | 6 | 2 | 5 | 6 | 5 | 5 | 1 | 5 | 1 | 6 | 1 | 2 | 6 | 6 |

the Polymers and Resins Studied

| P | Q | R | S | T | U | V | X | Y | Z | $\bar{A}$ | $\bar{B}$ | $\bar{C}$ | $\bar{D}$ | $\bar{E}$ | $\bar{F}$ | $\bar{G}$ | $\bar{L}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 5 | 4 | 1 | 6 | 5 | 6 | 6 | 6 | 5 | 6 | 1 | 6 | 5 | 6 | 6 | 6 | 5 |
| 1 | 5 | 5 | 1 | 6 | 6 | 6 | 6 | 6 | 5 | 5 | 1 | 6 | 5 | 6 | 6 | 6 | 5 |
| 1 | 5 | 4 | 1 | 6 | 6 | 6 | 6 | 6 | 6 | 4 | 1 | 6 | 5 | 6 | 6 | 6 | 6 |
| 1 | 6 | 4 | 2 | 6 | 6 | 6 | 1 | 5 | 1 | 5 | 1 | 6 | 4 | 6 | 6 | 6 | 6 |
| 1 | 6 | 4 | 3 | 6 | 6 | 6 | 1 | 5 | 1 | 3 | 1 | 6 | 4 | 6 | 6 | 6 | 6 |
| 1 | 6 | 5 | 6 | 6 | 6 | 6 | 1 | 6 | 1 | 1 | 1 | 6 | 4 | 6 | 6 | 6 | 6 |
| 1 | 6 | 3 | 3 | 6 | 6 | 6 | 1 | 6 | 1 | 1 | 1 | 5 | 4 | 6 | 6 | 6 | 6 |
| 1 | 6 | 4 | 4 | 6 | 6 | 5 | 1 | 5 | 1 | 1 | 1 | 1 | 4 | 5 | 6 | 6 | 6 |
| 1 | 6 | 4 | 4 | 6 | 5 | 6 | 1 | 6 | 1 | 1 | 1 | 5 | 4 | 6 | 6 | 6 | 6 |
| 4 | 6 | 5 | 1 | 6 | 6 | 6 | 6 | 6 | 6 | 6 | 1 | 6 | 5 | 6 | 6 | 6 | 3 |
| 6 | 6 | 5 | 2 | 6 | 4 | 6 | 6 | 5 | 6 | 6 | 6 | 6 | 6 | 6 | 6 | 6 | 1− |
| 1 | 4 | 6 | 1 | 5 | 5 | 6 | 6 | 6 | 6 | 6 | 1 | 6 | 6 | 6 | 6 | 6 | 6 |
| 6 | 6 | 4 | 3 | 6 | 6 | 5 | 6 | 6 | 6 | 6 | 6 | 6 | 6 | 6 | 6 | 6 | 6 |
| 1 | 5 | 2 | 1 | 5 | 5 | 5 | 1 | 5 | 1 | 1 | 1 | 5 | 1 | 6 | 6 | 5 | 6 |
| 1 | 1 | 1 | 1 | 5 | 1 | 5 | 1 | 5 | 1 | 1 | 1 | 6 | 1 | 6 | 6 | 1 | 1 |
| 1 | 1 | 1 | 1 | 6 | 4 | 6 | 6 | 6 | 6 | 3 | 1 | 6 | 1 | 6 | 6 | 5 | 3 |
| 1 | 3 | 1 | 1 | 6 | 1 | 6 | 5 | 6 | 3 | 1 | 1 | 6 | 1 | 6 | 6 | 1 | 6 |
| 1 | 1 | 5 | 1 | 6 | 6 | 6 | 6 | 6 | 6 | 6 | 1 | 6 | 1 | 6 | 6 | 6 | 1 |
| 1 | 1 | 5 | 1 | 6 | 6 | 6 | 6 | 6 | 6 | 6 | 1 | 6 | 1 | 6 | 6 | 6 | 1 |
| 1 | 1 | 1 | 1 | 6 | 4 | 6 | 1 | 6 | 4 | 1 | 1 | 6 | 1 | 6 | 6 | 1 | 6 |
| 1 | 1 | 1 | 1 | 6 | 3 | 6 | 6 | 6 | 6 | 5 | 1 | 6 | 1 | 6 | 6 | 4 | 1 |
| 1 | 1 | 1 | 1 | 6 | 4 | 5 | 5 | 6 | 6 | 1 | 1 | 6 | 1 | 6 | 6 | 1 | 1+ |
| 1 | 1 | 1 | 1 | 6 | 4 | 6 | 6 | 6 | 6 | 1 | 1 | 6 | 1 | 6 | 6 | 2 | 1− |
| 1 | 1 | 1 | 1 | 6 | 1 | 6 | 6 | 6 | 6 | 1 | 1 | 6 | 1 | 6 | 6 | 5 | 1− |
| 1 | 1 | 1 | 1 | 5 | 1 | 6 | 6 | 6 | 6 | 1 | 1 | 6 | 1 | 6 | 5 | 1 | 6 |
| 1 | 1 | 1 | 1 | 6 | 5 | 6 | 6 | 6 | 6 | 4 | 1 | 6 | 1 | 6 | 6 | 5 | 1+ |
| 3 | 6 | 5 | 3 | 1 | 6 | 1 | 1 | 1 | 6 | 1 | 1 | 1 | 4 | 1 | 6 | 1 | 6 |
| 5 | 5 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 6 | 1 | 1 | 1 | 4 | 1 | 6 | 1 | 6 |
| 1 | 1 | 1 | 1 | 1 | 1 | 4 | 5 | 1 | 6 | 1 | 1 | 4 | 1 | 5 | 3 | 1 | 2 |
| 1 | 5 | 1 | 1 | 5 | 1 | 4 | 1 | 3 | 6 | 1 | 1 | 5 | 2 | 3 | 6 | 1 | 6 |
| 5 | 6 | 1 | 4 | 1 | 1 | 1 | 1 | 1 | 6 | 1 | 1 | 1 | 4 | 1 | 6 | 1 | 6 |
| 5 | 4 | 3 | 3 | 1 | 4 | 1 | 1 | 1 | 4 | 1 | 1 | 1 | 6 | 1 | 6 | 1 | 4 |
| 1 | 1 | 1 | 1 | 6 | 5 | 6 | 6 | 6 | 6 | 6 | 1 | 6 | 1 | 6 | 2 | 6 | 1+ |
| 6 | 1 | 1 | 1 | 6 | 4 | 6 | 6 | 6 | 6 | 6 | 1 | 6 | 1 | 6 | 6 | 6 | 6 |
| 1 | 1 | 1 | 1 | 6 | 1 | 6 | 6 | 6 | 6 | 5 | 1 | 6 | 1 | 6 | 4 | 2 | 1+ |
| 1 | 1 | 1 | 1 | 6 | 1 | 6 | 6 | 6 | 6 | 1 | 1 | 6 | 1 | 6 | 5 | 2 | 5 |
| 1 | 1 | 1 | 1 | 4 | 1 | 4 | 1 | 4 | 6 | 1 | 1 | 5 | 1 | 5 | 3 | 1 | 6 |
| 1 | 4 | 1 | 1 | 1 | 1 | 1 | 1 | 4 | 6 | 1 | 1 | 1 | 4 | 4 | 4 | 1 | 6 |
| 1 | 6 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 6 | 1 | 1 | 1 | 4 | 2 | 5 | 1 | 6 |
| 2 | 6 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 6 | 1 | 1 | 1 | 6 | 1 | 6 | 1 | 6 |
| 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 6 | 1 | 1 | 1 | 1 | 5 | 2 | 1 | 5 |
| 1 | 1 | 1 | 1 | 1 | 1 | 5 | 5 | 2 | 6 | 1 | 1 | 5 | 1 | 5 | 2 | 1 | 4 |
| 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 6 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 5 |
| 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 3 |
| 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 6 | 1 | 1 | 1 | 1 | 4 | 2 | 1 | 4 |
| 1 | 1 | 1 | 1 | 3 | 1 | 5 | 1 | 5 | 6 | 1 | 1 | 4 | 1 | 4 | 6 | 1 | 6 |
| 1 | 6 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 6 | 1 | 1 | 1 | 2 | 1 | 5 | 1 | 6 |
| 5 | 6 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 6 | 1 | 1 | 1 | 4 | 1 | 5 | 1 | 6 |
| 6 | 6 | 1 | 3 | 1 | 1 | 1 | 1 | 1 | 6 | 1 | 1 | 1 | 5 | 1 | 6 | 1 | 6 |
| 6 | 5 | 2 | 1 | 6 | 5 | 6 | 6 | 6 | 6 | 4 | 1 | 6 | 4 | 6 | 6 | 5 | 6 |
| 4 | 5 | 1 | 1 | 6 | 1 | 5 | 6 | 6 | 6 | 1 | 1 | 6 | 2 | 6 | 6 | 1 | 5 |
| 6 | 5 | 2 | 1 | 6 | 1 | 6 | 6 | 6 | 6 | 4 | 1 | 6 | 4 | 6 | 6 | 5 | 6 |

Table 2.3

| | | A | B | C | D | E | F | G | H | I | J | K | L | M | N | ● |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 40 | Nitroethane | 1 | 1 | 1 | 1 | 5 | 5 | 2 | 1 | 6 | 1 | 5 | 5 | 1 | 6 | 3 |
| 41 | 2-Nitropropane | 1 | 1 | 2 | 1 | 6 | 5 | 1 | 1 | 6 | 1 | 3 | 5 | 1 | 6 | 4 |
| 42 | Aniline | 1 | * | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 3 | 1 | 3 | 1 | 1 | 1 |
| 43 | Nitrobenzene | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 4 | 1 | 5 | 1 |
| 44 | Ethanolamine | 6 | 6 | 1 | 6 | 2 | 6 | 6 | 6 | 5 | * | * | 4 | 1 | 1 | 5 |
| 45 | Dimethyl formamide | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| 46 | Dipropyl amine | 1 | 6 | 1 | 1 | 1 | 1 | 1 | 5 | 6 | 5 | 5 | 6 | 1 | 1 | 1 |
| 47 | Diethyl amine | 1 | 6 | 1 | 1 | 1 | 1 | 1 | 5 | 4 | * | 5 | 6 | 1 | 1 | 1 |
| 47A | Morpholine | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| 47B | Cyclohexylamine | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | * | * | 3 | 1 | 1 | 1 |
| 47C | Pyridine | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| 48 | Carbon tetrachloride | 1 | 5 | 4 | 1 | 2 | 5 | 1 | 1 | 6 | 6 | 1 | 6 | 1 | 6 | 1 |
| 49 | Chloroform | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 6 | 1 | 3 | 1 | 6 | 1 |
| 50 | Ethylene chloride | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 6 | 1 | 5 | 1 | 6 | 1 |
| 51 | Methylene chloride | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 6 | 1 | 5 | 1 | 6 | 1 |
| 52 | 1,1,1 Trichloroethane | 1 | 5 | 4 | 1 | 1 | 4 | 1 | 1 | 6 | 6 | 1 | 6 | 1 | 6 | 1 |
| 52A | 1-Chlorobutane | 1 | 4 | 2 | 1 | 1 | 4 | 1 | 1 | 3 | 6 | 1 | 6 | 1 | 6 | 1 |
| 53 | Trichloroethylene | 1 | 4 | 2 | 1 | 1 | 1 | 1 | 1 | 1 | 6 | 1 | 6 | 1 | 6 | 1 |
| 53A | 2,2 Dichloro diethyl ether | 1 | 1 | 1 | 1 | 5 | 3 | 1 | 1 | 5 | 5 | 1 | 5 | 1 | 6 | 1 |
| 54 | Chlorobenzene | 1 | 1 | 2 | 1 | 1 | 1 | 1 | 1 | 1 | 6 | 1 | 6 | 1 | 6 | 1 |
| 55 | o-Dichlorobenzene | 1 | 1 | 2 | 1 | 1 | 1 | 1 | 1 | 2 | 6 | 1 | 6 | 1 | 6 | 1 |
| 56 | α-bromonaphthaline | 1 | 6 | 2 | 1 | 1 | 1 | 1 | 1 | 6 | 6 | 1 | 6 | 1 | 6 | 1 |
| 56A | Cyclohexylchloride | 1 | 3 | 4 | 1 | 1 | 4 | 1 | 4 | 5 | 6 | 1 | 6 | 1 | 6 | 1 |
| 57 | Benzene | 1 | 5 | 1 | 1 | 1 | 1 | 1 | 1 | 5 | 6 | 1 | 6 | 1 | 6 | 1 |
| 58 | Toluene | 1 | 2 | 2 | 1 | 1 | 2 | 1 | 1 | 2 | 6 | 1 | 6 | 1 | 6 | 1 |
| 58A | Xylene | 1 | 4 | 3 | 1 | 5 | 3 | 1 | 4 | 5 | 5 | 1 | 6 | 1 | 6 | 1 |
| 59 | Ethyl benzene | 1 | 5 | 4 | 1 | 2 | 3 | 1 | 1 | 4 | 6 | 1 | 6 | 1 | 6 | 1 |
| 60 | Styrene | 1 | 2 | 2 | 1 | 1 | 1 | 1 | 1 | 3 | 6 | 1 | 6 | 1 | 6 | 1 |
| 61 | Tetralin | 1 | 3 | 4 | 1 | 1 | 2 | 1 | 5 | 5 | 6 | 1 | 6 | 1 | 6 | 1 |
| 62 | Hexane | 6 | 5 | 6 | 1 | 6 | 6 | 3 | 6 | 6 | 6 | 6 | 6 | 1 | 6 | 5 |
| 63 | Cyclohexane | 6 | 6 | 6 | 1 | 6 | 5 | 1 | 4 | 6 | 6 | 6 | 6 | 1 | 6 | 1 |
| 65 | Acetic acid | 1 | 6 | 1 | 4 | 2 | 1 | 6 | 1 | 1 | 1 | 6 | 3 | 1 | 4 | 4 |
| 67 | Formic acid (90%) | 1 | 6 | 5 | 3 | 6 | 1 | 6 | 1 | 1 | 6 | 6 | 1 | 5 | 1 | 5 |
| 67A | Butyric acid | 1 | 6 | 1 | 1 | 1 | 1 | 4 | 1 | 1 | 6 | 6 | 6 | 1 | 6 | 1 |
| 68 | Benzaldehyde | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 4 | 1 | 1 | 1 |
| 69 | Acetic anhydride | 1 | 5 | 1 | 3 | 2 | 5 | 6 | 1 | 1 | 1 | 6 | 1 | 1 | 1 | 5 |

* Reaction

+ Unidentified particles in solution

Thus,

$$\delta_H = \sqrt{\frac{5000\,A}{V_m}} \tag{2.19}$$

where A is the number of alcohol groups in the molecule.

A plot of these calculated $\delta_H$ values versus the revised placements of solvents along the hydrogen bonding axis, $\delta_h$, is given in Figure 2.2.

(continued)

| P | Q | R | S | T | U | V | X | Y | Z | $\bar{A}$ | $\bar{B}$ | $\bar{C}$ | $\bar{D}$ | $\bar{E}$ | $\bar{F}$ | $\bar{G}$ | $\bar{L}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 6 | 5 | 1 | 1 | 6 | 1 | 6 | 6 | 6 | 6 | 3 | 1 | 6 | 3 | 6 | 6 | 2 | 6 |
| 6 | 4 | 1 | 1 | 6 | 1 | 6 | 6 | 5 | 6 | 1 | 1 | 6 | 3 | 6 | 5 | 1 | 6 |
| 1 | 1 | 1 | 1 | 6 | 1 | 6 | 6 | 6 | 5 | 1 | 1 | 6 | 1 | 6 | 3 | 1 | 1 |
| 3 | 2 | 1 | 1 | 1 | 1 | 1 | 6 | 1 | 6 | 1 | 1 | 5 | 1 | 6 | 2 | 1 | 4 |
| 1 | 5 | 6 | 1 | 6 | 6 | 6 | 6 | 5 | 6 | 6 | 6 | 6 | 1 | 6 | 6 | 6 | 1+ |
| 1 | 1 | 1 | 1 | 6 | 1 | 5 | 5 | 6 | 6 | 4 | 1 | 6 | 1 | 6 | 4 | 1 | 1+ |
| 5 | 5 | 1 | 2 | 1 | 4 | 1 | 1 | 1 | 6 | 1 | 1 | 1 | 3 | 1 | 6 | 1 | 6 |
| 5 | 5 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 5 | 1 | 1 | 1 | 2 | 1 | 6 | 1 | 5 |
| 1 | 1 | 1 | 1 | 4 | 1 | 5 | 4 | 5 | 6 | 1 | 1 | 6 | 1 | 6 | 1 | 1 | 1 |
| 5 | 6 | 1 | * | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 6 | 1 | * |
| 1 | 1 | 1 | 1 | 1 | 1 | 5 | 4 | 1 | 5 | 1 | 1 | 5 | 1 | 5 | 2 | 1 | 1 |
| 5 | 6 | 1 | 5 | 1 | 5 | 1 | 1 | 1 | 4 | 1 | 1 | 1 | 4 | 1 | 6 | 1 | 5 |
| 3 | 3 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 5 | 1 | 6 |
| 4 | 5 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 6 | 1 | 1 | 1 | 1 | 2 | 3 | 1 | 6 |
| 5 | 3 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 2 | 1 | 1 | 1 | 1 | 1 | 2 | 1 | 6 |
| 3 | 6 | 1 | 3 | 1 | 1 | 1 | 1 | 1 | 6 | 1 | 1 | 1 | 4 | 1 | 6 | 1 | 6 |
| 3 | 6 | 1 | 3 | 1 | 1 | 1 | 1 | 1 | 5 | 1 | 1 | 1 | 3 | 1 | 6 | 1 | 6 |
| 4 | 5 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 2 | 1 | 1 | 1 | 4 | 1 | 5 | 1 | 5 |
| 6 | 5 | 1 | 1 | 5 | 1 | 6 | 6 | 5 | 6 | 1 | 1 | 4 | 1 | 6 | 3 | 1 | 6 |
| 5 | 6 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 5 | 1 | 1 | 1 | 3 | 1 | 4 | 1 | 5 |
| 4 | 6 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 6 | 1 | 1 | 1 | 3 | 1 | 4 | 1 | 4 |
| 6 | 6 | 1 | 4 | 1 | 1 | 1 | 5 | 1 | 6 | 1 | 1 | 1 | 5 | 1 | 4 | 1 | 4 |
| 6 | 6 | 1 | 4 | 1 | 1 | 1 | 1 | 1 | 6 | 1 | 1 | 1 | 3 | 1 | 5 | 1 | 6 |
| 6 | 6 | 1 | 2 | 1 | 1 | 1 | 1 | 1 | 5 | 1 | 1 | 1 | 4 | 1 | 5 | 1 | 5 |
| 6 | 6 | 1 | 3 | 1 | 1 | 1 | 1 | 1 | 6 | 1 | 1 | 1 | 5 | 1 | 5 | 1 | 5 |
| 6 | 6 | 1 | 3 | 1 | 1 | 1 | 1 | 1 | 6 | 1 | 1 | 1 | 5 | 1 | 6 | 1 | 6 |
| 6 | 6 | 1 | 3 | 1 | 1 | 1 | 1 | 1 | 6 | 1 | 1 | 1 | 6 | 1 | 6 | 1 | 6 |
| 4 | 6 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 6 | 1 | 1 | 1 | 4 | 1 | 5 | 1 | 5 |
| 4 | 6 | 1 | 2 | 1 | 1 | 1 | 1 | 1 | 5 | 1 | 1 | 1 | 5 | 1 | 6 | 1 | 4 |
| 5 | 6 | 5 | 6 | 3 | 6 | 1 | 1 | 1 | 6 | 4 | 6 | 1 | 6 | 2 | 6 | 5 | 6 |
| 5 | 6 | 5 | 5 | 1 | 6 | 1 | 1 | 1 | 6 | 2 | 4 | 1 | 6 | 1 | 6 | 2 | 6 |
| 1 | 4 | 1 | 1 | 6 | 6 | 6 | 6 | 6 | 3 | 4 | 1 | 6 | 1 | 6 | 6 | 5 | 4 |
| 6 | 2 | 5 | 1 | 6 | 6 | 6 | 6 | 6 | 3 | 6 | 1 | 6 | 6 | 6 | 6 | 6 | 1+ |
| 1 | 6 | 1 | 1 | 4 | 5 | 4 | 1 | 4 | 1 | 1 | 1 | 1 | 3 | 4 | 6 | 1 | 6 |
| 1 | 1 | 1 | 1 | 2 | 1 | 5 | 5 | 4 | 3 | 1 | 1 | 5 | 1 | 4 | 1 | 1 | 3 |
| 1 | 4 | 1 | 1 | 6 | 2 | 6 | 6 | 6 | 6 | 5 | 1 | 5 | 1 | 5 | 6 | 5 | 5 |

## 2.7 *Correlation with Polar Bonding*

Böttcher (1952) has developed a relation for calculating the contribution of the permanent dipoles to the cohesion energy of a liquid or a gas. This energy is given as W in Equation 2.20 and has been divided by $V_m$ to fit the definition of the polar solubility parameter as given in Equation 2.21.

2.20) $$W = \frac{-4\pi}{3} \cdot \frac{dN_A^2}{M} \cdot \frac{\varepsilon - 1}{2\varepsilon + n_D^2} \cdot \frac{n_D^2 + 2}{3} \mu^2 \left[\frac{\text{erg}}{\text{mole}}\right]$$

2.21) $$\frac{W}{V} = \delta_P^2 = \frac{12108}{V_m^2} \frac{\varepsilon - 1}{2\varepsilon + n_D^2} (n_D^2 + 2) \mu^2 \left[\frac{\text{cal}}{\text{cm}^3}\right]$$

Table 2.4

Approximate Components of the Solubility Parameter for Plasticizers

| Plasticizer | $\delta_d$ | $\delta_p$ | $\delta_h$ |
|---|---|---|---|
| TCP-Tricresyl phosphate | 9.3 | 6.0 | 2.2 |
| DMP-Dimethyl phthalate | 8.3 | 6.5 | 2.4 |
| DBP-Dibutyl phthalate | 8.2 | 4.2 | 2.0 |
| DOP-Dioctyl phthalate | 8.1 | 3.4 | 1.5 |
| BBP-Butyl benzyl phthalate | 9.3 | 5.5 | 1.5 |
| Citroflex® 4 | 7.9 | 1.5 | 4.5 |
| Citroflex® A-4 | 7.5 | 2.0 | 3.0 |
| DBM-Dibutyl maleate | 7.5 | 1.5 | 3.5 |
| DOA-Dioctyl adipate | 7.4 | 1.0 | 2.0 |
| TOP-Trioctyl phosphate | 8.0 | 1.0 | 2.5 |

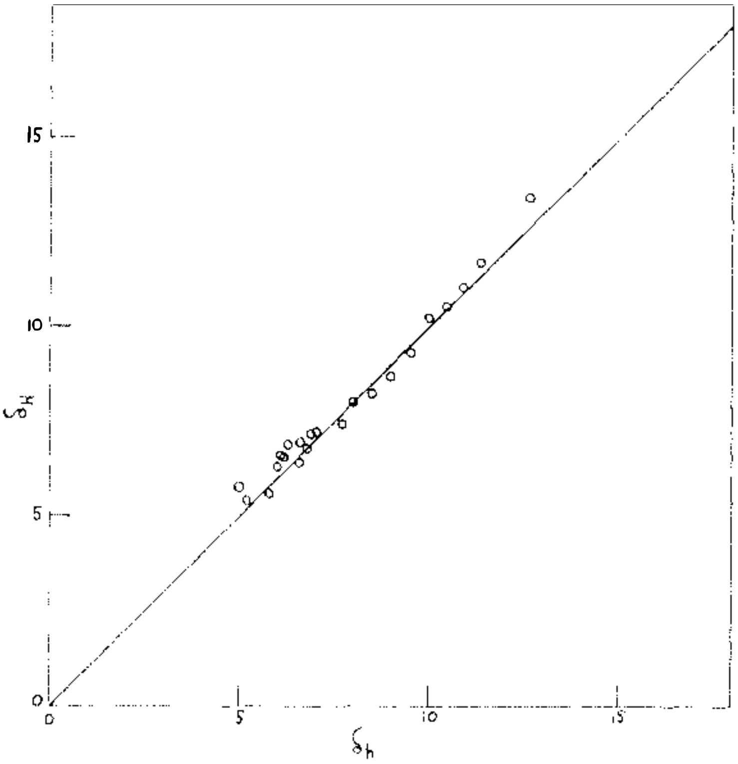


Figure 2.2. The correlation between $\delta_H$ and $\delta_h$

The symbols used are for the condensed phase with:

d = density, g/cm$^3$
M = molecular weight
$N_A$ = Avogadros number
$\varepsilon$ = dielectric constant, static value
$n_D$ = index of refraction for sodium—D line
$\mu$ = dipole moment, Debyes in Eqn. 2.21; e.s.u. in Eqn. 2.20
$V_m$ = molar volume, cm$^3$

Values for these constants were found in standard references (Landolt-Börnstein, Weast 1964) for 65 solvents. The corresponding values of $\delta_P$ were found from Equation 2.21 and are included in Table 2.1 and Figure 2.3 for comparison with the revised placements of the solvents along the polar solubility parameter axis, $\delta_p$, in the system.

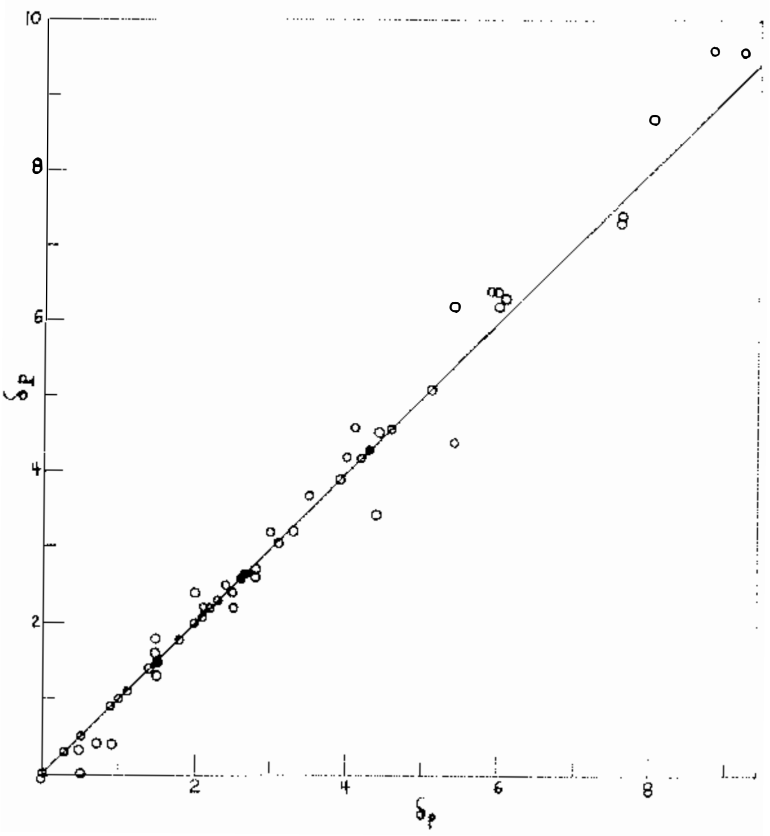


Figure 2.3. The correlation between $\delta_P$ and $\delta_p$

The model for Equation 2.20 was a spherical molecule with the dipole center at the center of the molecule. The extent to which this idealized model can be in error has been calculated (Böttcher 1952) for the situation where the center of the dipole is removed a distance s from the center of the spherical molecule of radius a. $\delta_P^2$ must be multiplied by the values listed in Table 2.5 for these cases. Errors can also be expected for molecules which deviate significantly from the spherical model.

Table 2.5

Correction Factor for $\delta_P^2$ for Molecules where the Center of the Dipole is Not at the Center of the Molecule. (Böttcher 1952)

| | $\varepsilon = 2$ | $\varepsilon = 6$ |
|---|---|---|
| s/a = .1 ................ | 1.04 | 1.04 |
| s/a = .25 ................ | 1.27 | 1.28 |
| s/a = .50 ................ | 2.8 | 2.90 |

For some solvents, particularly 2,2 dichloro diethyl ether and acetic anhydride, the values found from Equation 2.21 appear to be low. The values of $\delta_P$ reported for these solvents have been chosen to agree with solubility data. $\delta_P$ for dimethyl phthalate is calculated as 2.5 which is significantly below the $\delta_p$ of 6.5 estimated from solubility data. Steric considerations would seem to require an increase of $\delta_P$ by some factor in accord with the removal of the dipole from the center of the molecule, so this seeming discrepancy is not considered serious. All three of these materials are symmetric.

## 2.8 *Permanent Dipole-Induced Dipole Interactions*

Carbon tetrachloride and carbon disulfide appear to have some polar activity at times. This may well be attributed to permanent dipole-induced dipole interactions. The cohesive energy arising from induced dipoles has not been included explicitly in the development of the three dimensional solubility parameter system.

Since these energies are relatively weak, this fact affects neither the system's general usefulness nor the relative placements of the solvents. They can become significant when $\delta_p$ for a solvent is zero or close to zero.

## 2.9 *Conclusion*

In what is to follow, solvents will be called points in the system, just like polymers can be thought of as volumes in the system. Even solvent mixtures are included in the general term "solvents" and can be thought of as points. This is justified by the foregoing. Other solvents can be added to the system. This can be done either by calculation, where possible, or by solubility experiments alone, but preferably by a combination of the two.

It is interesting to note that early studies by Brønsted (Brønsted 1938, Brønsted and Volquartz 1939, 1940) contain results which are directly related to the present study. The phenomenon that two non-solvents could dissolve a polymer is clearly demonstrated on triangular solubility plots. Studies were also performed to predict solubility relationships in mixtures of the members in a homologous series (Brønsted and Koefoed 1946, Koefoed 1953). As the molecular weight increased in the series composed of the esters of lauric acid, the effect on polystyrene became less. Solubility was found for ethyl laurate but not for propyl laurate and swelling decreased for the higher members of the series. This demonstrates the decrease of $\delta_a$ with higher molecular weights in a homologous series with the result that eventually the placement of a given solvent lies outside of the volume of solubility for a given solute. $V_m$ also has an effect.

In his studies, Brønsted was looking for a generalization for solubility behavior based on solvent properties. The present study would appear to represent the most advanced state the generalization of solvent behavior has attained to date.

The whole treatment of the solubility parameter in this volume is at very best semi-empirical; no real theory has been developed. Chapter 3 and particularly Chapter 4 are, therefore, written primarily for those who must use the concept in practice.

## Chapter 3

# The Characterization of Non-ionic Emulsifiers, Dyes and Pigments

### 3.1 *Introduction*

Being able to characterize solvents, plasticizers, and polymers and resins by the same parameter is, in itself, a practical help in solvent selection. The solubility parameter system shows all the possibilities of solvent combinations available to the formulator in a systematic manner even though many of these are not practical because of cost, odor, slow evaporation, reactivity, etc. The usefulness of the system does not stop here, non-ionic emulsifiers, dyes, and pigments have been characterized by the same system.

### 3.2 *Non-ionic Emulsifiers*

Non-ionic emulsifiers have essentially the same type solubility properties as polymers. Solubility data obtained for 12 emulsifiers indicate they can be characterized by volumes formed by the points representing the solvents which dissolve them. Mixtures of non-solvents dissolved the non-ionic emulsifiers tested when the individual solvents were located on opposite sides of the emulsifier volume of solubility from each other. This is analogous to polymers and resins and shows they are characterized by the three dimensional solubility parameter.

The use of the HLB system indicated in advance that the solubility parameter could be used to describe emulsifiers (Weidner 1965, Pascal and Reig 1964). The HLB system derives its name since it describes an emulsifier in terms of a "hydrophile-lipophile balance" (water loving—oil loving balance). The HLB number of an emulsifier is calculated as the percent of the hydrophilic portion of its molecule (ethylene oxide) divided by 5. This number has been used in practice to help in emulsifier selection.

### 3.3 *Dyes*

Some dyes are soluble in many organic solvents. This in itself would indicate the applicability of the solubility parameter to their characterization. Nine dyes of varying chemical constitution were shown to have solubility properties of the nature discussed above. The solvents which dissolved them at a given concentration defined a volume of solubility in the system, and mixtures of non-solvents could be chosen predictably such that they dissolved the dyes. The non-solvents need only lie on opposing sides of the region of solubility for a given solute.

### 3.4 *Pigments*

Pigments have also been characterized by the solubility parameter system. It is not the bulk of the pigment which is characterized, but rather the pigment surface. Since pigment surfaces are usually modified in some manner, it is difficult to say the characteristics of one pigment are the same as those of another even though their bulk composition is the same.

Pigment surfaces have been characterized by shaking a small amount of pigment in a test tube (about 0.1 g. for organic pigments) with 5 ml. of each of 53 solvents distributed throughout the system. The settling tendencies and color of the supernatant liquids were noted. Where complete suspension is found after a significant period of time, there can be no doubt in the judgment that there is interaction. Color in the supernatant liquid can arise from suspended "fines" as well as from bulk solubility. The eye can not always distinguish this, emphasizing the subjective nature of this type testing. Chemical reactions, solvent and pigment densities, solvent viscosity, initial pigment dispersion and size, adsorbed moisture, and numerous other factors can, and do, affect this most simple type testing. These factors apparently become insignificant to the overall picture since each of the pigments listed in Table 4.2 could be characterized by the parameters listed in Table 4.3. Interaction plots for a pigment are given in Figures 4.10, 4.11, and 4.12.

Those solvents which suspend a given pigment for a significant period of time will be found to define a volume of interaction for the pigment in the solubility parameter system. Non-suspending solvents can be mixed predictably to give a mixture which suspends the pigment. The individual solvents need only lie on opposite sides of the volume of interaction for the pigment. The degree of suspension in these cases is not always that which might have been expected from the data on pure liquids, however.

A number of pigments, particularly inorganic pigments, settle rapidly without suspending in any solvents. It is presumed that their surface energies lie too far from those capable of description by organic solvents to be described by them. Some inorganic pigments could be characterized, however. Inorganic pigments often have high densities, meaning somewhat stronger interactions are necessary to suspend them for a comparable particle size. If there are no small particles in the initial pigment sample, no prolonged suspension can be expected. Other means can be used to characterize pigment surfaces (Weisberg 1962); the present method has been chosen because a large number of observations can be made simultaneously, because of its simplicity, and because it apparently reflects the degree of interaction in a manner which has relevance to practical applications.

A significant period of suspension for a characterization varies from pigment to pigment. In many cases two or three days is long enough, particularly when the pigment settles rapidly in solvents with a viscosity of 100 cp. and remains suspended in solvents with a viscosity closer to 1 cp. Should the densities of the solvent and pigment be identical, the pigment will not settle. This is a very rare situation which can be accounted for in the evaluations. Numerous of the pigments float in carbon tetrachloride since its density is greater than their own. Many of the pigments are still suspended more than a year and a half after their initial suspension. In practice Stokes Law need not be considered as such in these tests of de-flocculation since there will invariably be some situation which indicates which of the solvents truly interact with the pigment surface. Most questionable points can be properly interpreted if a large number of solvents are used in the testing. The mathematics of settling in such systems have been discussed by Patton (1966).

## 3.5 *Pigment Charges*

Studies on the charge of pigments in various organic liquids have been published (Brintzinger et al. 1952, 1954, Hamann and Florus 1956). It is particularly noteworthy that the same pigments are often positive in alcohols and solvents near the hydrogen bonding axis, $\bar{\delta}_h$, and negative in acetone and nitrobenzene and solvents closer to the polar axis, $\bar{\delta}_p$.

Charge effects are also evident in pigment suspension measurements. Studies of the suspension characteristics of five alpha phthalocyanine blue pigments, characterized by electrophoretic mobilities at Køge Chemical Works (Vinther 1965, Petersen 1966), showed that those pigments listed as very strongly charged suspended in more solvents than the weakly charged pigments. The pigment labelled A++ had a large, well-defined suspension volume which tended toward the hydrogen bonding axis, while the pigment labelled as E− −(−) suspended for long times in solvents closer to the polar bonding axis, also yielding a well-defined volume. The pigments labelled as B++, C+, and D−− showed the same tendencies, but the volumes became less well-defined as the charge decreased.

## 3.6 *Conclusion*

The electrophoretic mobility of a pigment is related to testing where pigments are characterized by suspension measurements. Both these characterizations reflect the type of surface presented to the medium surrounding the pigment. The bulk properties of solvents, indicated by the solubility parameter, evidently reflect the character of the pigment surface through interactions with it. The solubility parameter can be divided into three components; this implies that the interfacial surface energy can also be divided into three components, though steric factors will be important in any correlation with the solubility parameter. See also Chapter 8.

Much more work with pigments is necessary to fully explain the phenomena discussed in this chapter.

*Chapter 4*

# Some Practical Aspects of the Three Dimensional Solubility Parameter

## 4.1 *Introduction*

The best empirical rule to remember when applying the solubility parameter to practical problems is still "like dissolves like". What has been done in this study is to better define just what this means. One need only remember that the more similar the solubility parameters of two materials, the more likely it is that they attract each other. The solubility parameter considered in the manner described here is actually closer to an attraction parameter.

That the solubility parameter has now been considered three dimensional should not present any special difficulties. The author has always worked with three dimensional models, while his colleague at the Danish Paint and Ink Research Laboratory, Mr. Klemen Skaarup, has shown there are distinct advantages to using the type two dimensional plots included in this chapter, at times using modelling clay to help portray a given point in the third dimension.

## 4.2 *General Considerations*

Anyone who has read the foregoing material will be thoroughly familiar with the concept that a solvent is identically equal to a point in the three dimensional solubility parameter system. Solvents dissolving a given solute form a volume of solubility in the system. Solvents dispersing or suspending a given pigment likewise form a volume of dispersion or suspension in the system. In other words, plot each of the interacting solvents in any convenient manner, and the plotted points will be seen to cluster in the system.

Furthermore, if plotting on paper is preferred, the length for each unit along the dispersion axis should be twice that for each unit along the polar or hydrogen bonding axis. This empirical convenience is suggested because of the symmetry of these plots; circles can be drawn to determine a center for a given volume of interaction. Plots of the type given in Figures 4.1, 4.2, and 4.3 for the solubility of poly(vinyl acetate) are suggested. The solubility data for poly(styrene) and cellulose nitrate have also been included graphically in Figures 4.4 through 4.9.

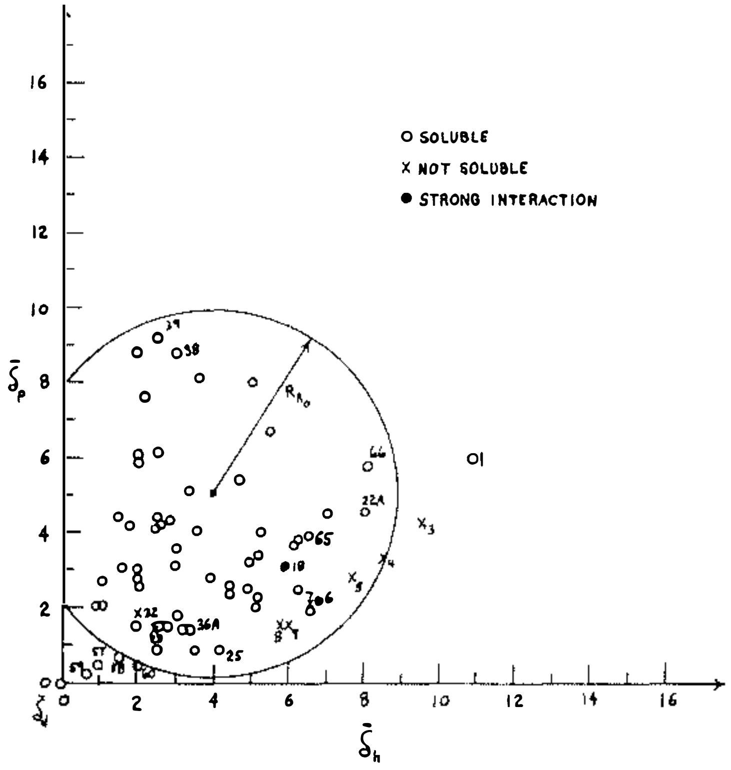


Figure 4.1. The solubility of poly(vinyl acetate)

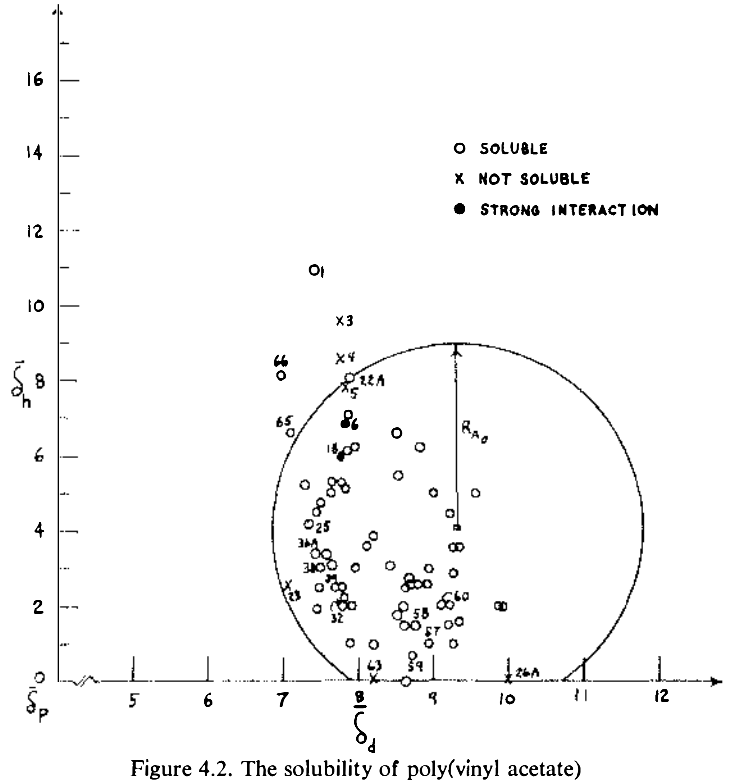


Figure 4.2. The solubility of poly(vinyl acetate)

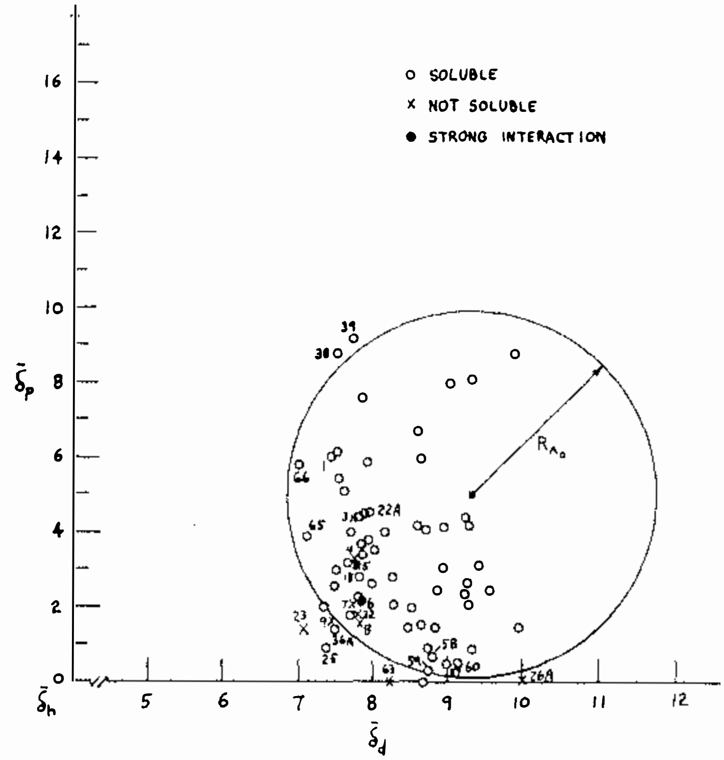


Figure 4.3. The solubility of poly(vinyl acetate)

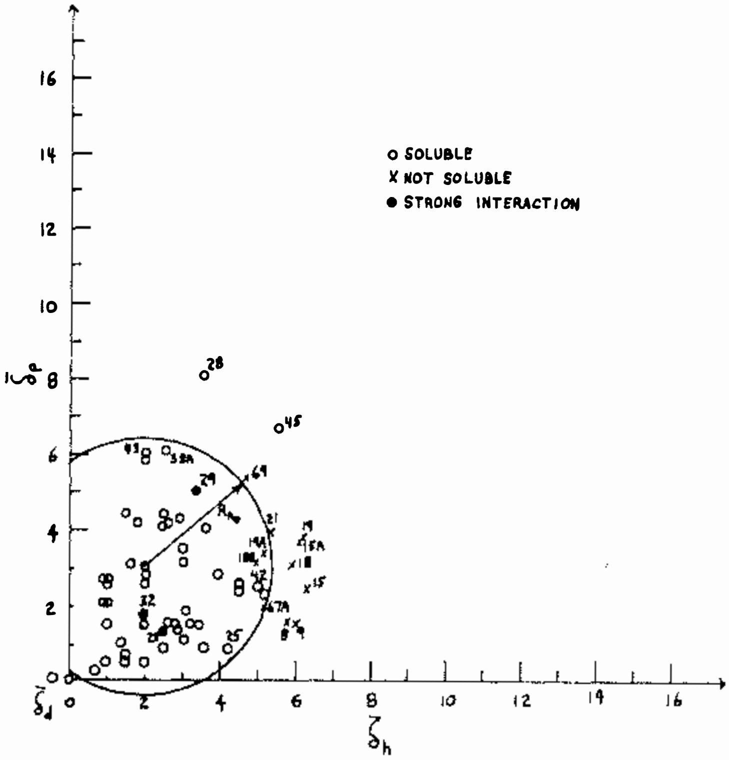


Figure 4.4. The solubility of poly(styrene)

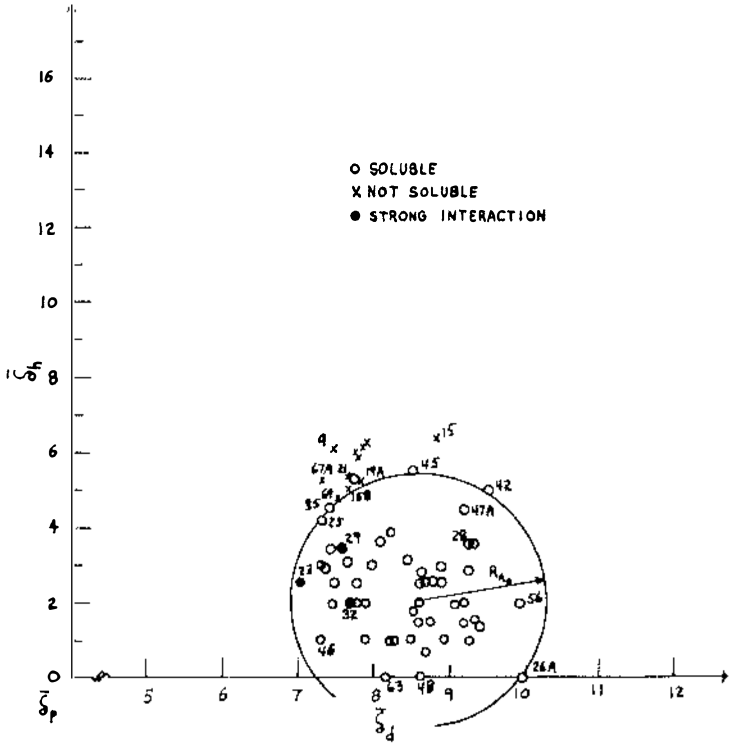


Figure 4.5. The solubility of poly(styrene)

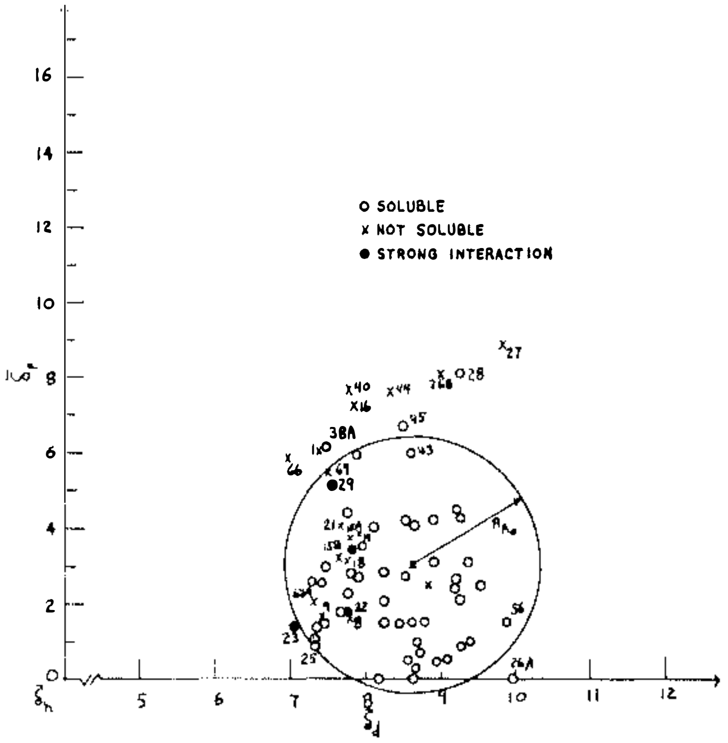


Figure 4.6. The solubility of poly(styrene)

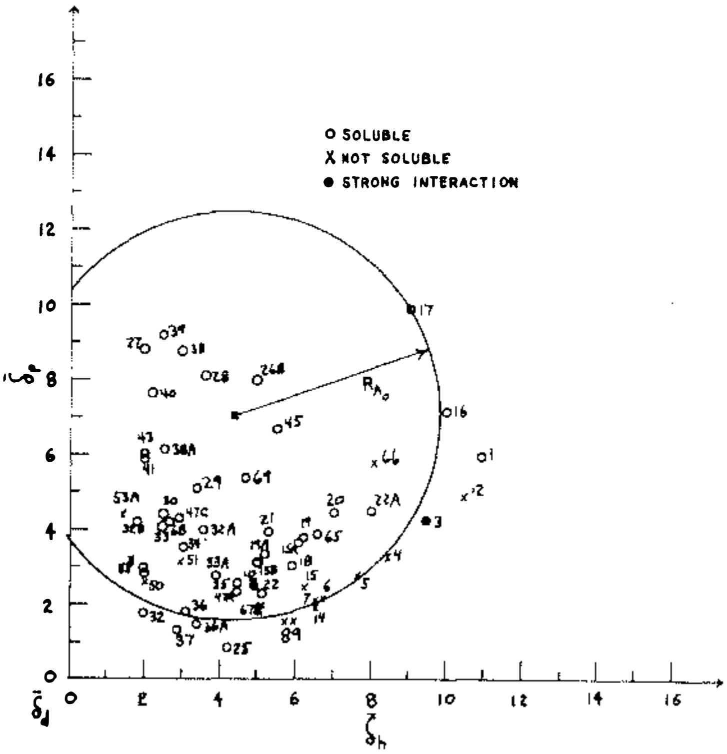


Figure 4.7. The solubility of cellulose nitrate

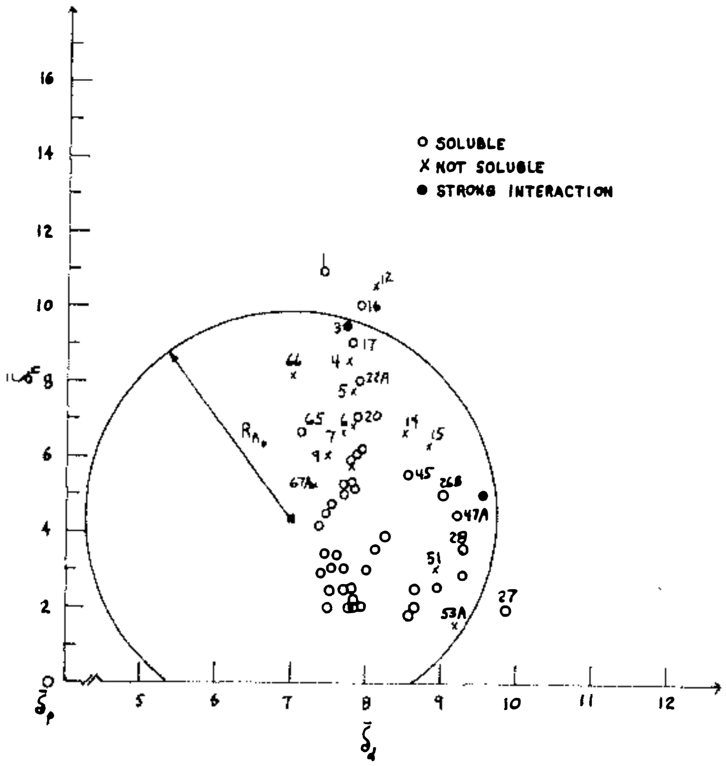


Figure 4.8. The solubility of cellulose nitrate

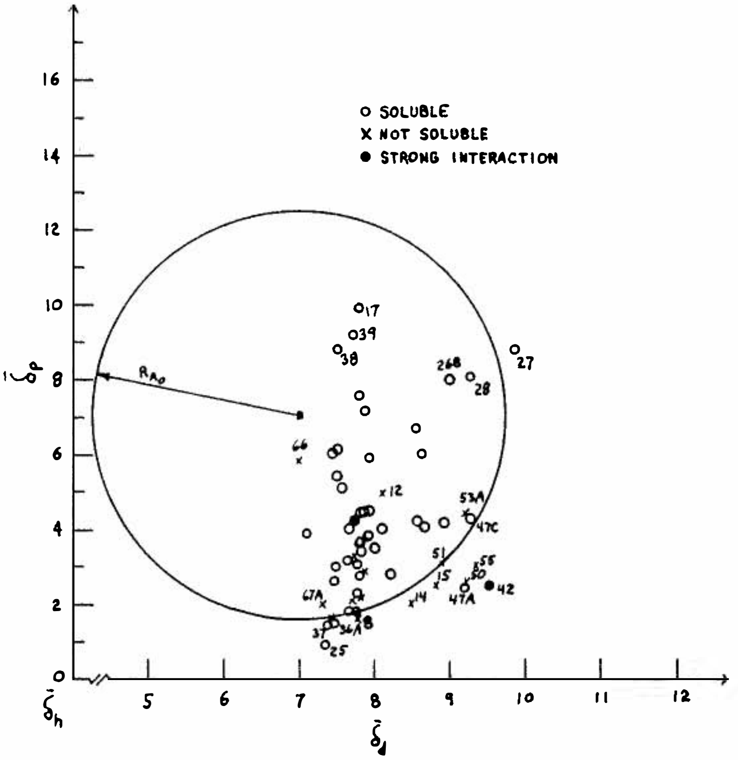


Figure 4.9. The solubility of cellulose nitrate

In several instances in the following the concept of improving solvent quality is used. Improving solvent quality means choosing a solvent closer to the center of the volume of solubility for a given solute. This need not be done by choosing an entirely new solvent. In many cases simply adding a quantity of solvent which is located in the direction one wants to move the solvent is fully sufficient. At times very small quantities of added solvent produce large effects, particularly if the added solvent is located far from the initial solvent, and if the initial solvent is in the boundary region of a given solute's volume of solubility. The added solvent need not dissolve the solute in its pure state to be effective in this manner.

It is assumed that no reactions occur in any of the systems described, and that solvent placements are additive on a volume fraction basis for solvent mixtures. Crystallinity in the solute has not been considered in this study.

## 4.3 *Solvents*

Solvents are located as points in the system according to their individual abilities to take part in interactions involving dispersion, polar, or hydrogen bonding forces. These locations, given in Table 2.1, have a certain degree of uncertainty. The characterizations will be more accurate if more solvents are used. The uncertainty for a solvent's placement varies with its location in the system but should be less than about 0.5 units. The placements of more remotely located solvents are less certain.

### 4.4 *Polymers*

Polymers have been characterized by volumes of solubility formed by all the solvents dissolving them. More stable solutions will be found with solvents closer to the centers of these volumes since these solvents will, in general, be better. Even absolute viscosities can at times be reduced by choosing solvents closer to the center of the solubility volumes (Sørensen 1967).

Mixtures of non-solvents which dissolve a given polymer can be predictably found. These solvents need only lie on opposing sides of the polymer's volume of solubility. If precipitation occurs on diluting a polymer solution with more solvent, it is obvious that the solvent lies in the boundary region of the polymer's volume of solubility. This can happen with alkyds and hydrocarbon solvents. This problem can be corrected by improving the solvent as described above. The cause of this precipitation is evidently due to a larger distribution of molecular weights in an alkyd resin, for example, which probably still contains some phthalic anhydride and low molecular weight components containing alcohol and acid groups. The lower molecular weight components in solution at high polymer concentration contribute to improving the quality of the solvent. On dilution their significance is decreased and the polymer precipitates if the solvent quality becomes too poor.

The centers of the volumes of solubility of the 33 polymers and resins studied have been determined as demonstrated in Figures 4.1 through 4.9. The characteristic parameters are given in Table 4.1. $R_{Ao}$ is defined by the distances indicated in these figures. These figures must be considered three at a time.

An average of about 2½ per cent of the solvents lying at a distance greater than $R_{Ao} + 0.5$ from the solute center can be expected to dissolve the solute. An average of about 2½ per cent of the solvents lying at a distance less than $R_{Ao} - 0.5$ from the solute center can be expected not to dissolve the solute. These are deviations from the most convenient plotting method found to date and do not affect the overall picture obtained by testing in this manner. These deviations generally occur in remote regions of the system. Methanol, with its low $V_m$, and solvents on the $\delta_d$ axis will at times dissolve a solute even though they lie outside of the volumes described by the circles. Slightly pear shaped volumes can be used in these cases if desired.

### 4.5 *Polymer Mixtures*

Many practical paint and varnish formulations involve two or more polymer or resin components. This situation has been studied for the simple case where the

Table 4.1
Characteristic Parameters for Polymers and Resins

| Solute | $\delta_0$ | $\delta_{d0}$ | $\delta_{p0}$ | $\delta_{h0}$ | $\delta_{a0}$ | $R_{A0}$ | Comments |
|---|---|---|---|---|---|---|---|
| A | 10.8 | 9.2 | 5.3 | 2.1 | 5.7 | 5.3 | |
| B | 11.3 | 9.2 | 5.0 | 4.2 | 6.5 | 4.0 | |
| C | 11.5 | 8.5 | 5.5 | 5.5 | 7.8 | 4.7 | |
| D | 9.4 | 8.5 | 2.5 | 3.0 | 3.9 | 5.3 | $\delta_d$ Arbitrary |
| E | 11.2 | 9.4 | 3.2 | 5.1 | 6.0 | 5.0 | Some deviations |
| F | 11.0 | 8.5 | 4.3 | 5.5 | 7.0 | 4.8 | |
| G | 9.8 | 8.6 | 3.0 | 2.0 | 3.6 | 3.5 | |
| H | 11.3 | 9.3 | 5.0 | 4.0 | 6.4 | 4.9 | A few deviations |
| I | 12.1 | 9.5 | 4.0 | 6.4 | 7.5 | 4.7 | |
| J | 10.8 | 7.0 | 7.0 | 4.3 | 8.2 | 5.5 | |
| K | 10.2 | 9.3 | 3.7 | 2.1 | 4.3 | 4.2 | |
| L | 12.7 | 9.5 | 6.0 | 6.0 | 8.5 | 4.5 | Radius of strong interaction |
| M | 11.3 | 9.0 | 4.0 | 5.5 | 6.8 | 6.4 | Too soluble, inaccurate |
| N | 13.1 | 9.4 | 5.3 | 7.4 | 9.1 | 5.5 | |
| O | 10.1 | 8.9 | 3.0 | 3.8 | 4.8 | 4.5 | |
| P | 11.7 | 8.5 | 4.7 | 6.5 | 8.0 | 5.0 | |
| Q | 12.1 | 9.3 | 6.2 | 4.7 | 7.8 | 4.2 | |
| R | 10.5 | 9.2 | 4.5 | 2.6 | 5.2 | 5.0 | |
| S | 12.5 | 8.8 | 7.0 | 5.5 | 8.9 | 6.0 | Low M.W. solute, liquid |
| T | 9.0 | 8.7 | 1.8 | 1.8 | 2.5 | 3.5 | |
| U | 10.5 | 9.3 | 4.5 | 2.0 | 4.9 | 4.7 | |
| V | 8.8 | 8.5 | 1.5 | 1.5 | 2.1 | 3.4 | |
| X | 8.6 | 7.8 | 1.0 | 3.5 | 3.6 | 4.0 | High M.W. rubber |
| Y | 9.2 | 8.8 | 2.5 | 1.2 | 2.8 | 3.8 | |
| Z | 10.2 | 8.2 | 0.8 | 5.7 | 3.2 | 2.9 | Some deviations |
| $\bar{A}$ | 9.7 | 8.7 | 2.5 | 3.5 | 4.3 | 4.2 | |
| $\bar{B}$ | 11.7 | 9.5 | 4.0 | 5.5 | 6.8 | 7.0 | Too soluble, inaccurate |
| $\bar{C}$ | 8.8 | 8.5 | 1.0 | 2.0 | 2.2 | 3.4 | |
| $\bar{D}$ | 11.6 | 9.2 | 5.8 | 4.2 | 7.2 | 5.0 | Liquid, hard to place |
| $\bar{E}$ | 8.8 | 8.5 | 1.5 | 1.8 | 2.3 | 2.6 | |
| $\bar{F}$ | 11.0 | 9.4 | 4.5 | 3.5 | 5.7 | 3.2 | Radius of strong interaction |
| $\bar{G}$ | 9.6 | 8.8 | 2.7 | 2.7 | 3.9 | 4.0 | |
| $\bar{L}$ | 15.6 | 10.8 | 7.0 | 8.8 | 11.2 | 7.1 | |

solubilities of equal weights of solutes were evaluated at 10 weight per cent solids (G). If one wants to dissolve two polymers simultaneously, the solvent chosen for this purpose must dissolve them both individually. This is equivalent to saying that the solvent must be located in the overlapping volume of solubility for the two polymers.

In a few cases, however, choosing a solvent in this overlapping region may not be sufficient. This is particularly true if one or both of the solutes has a high molecular weight. In this case the chances for mutual solubility can be improved by choosing a solvent of as good a quality as possible. Placing the solvent somewhat closer to the center of that component which is most difficult to dissolve is sometimes necessary, particularly when this component is of high molecular weight. The polymer which is most difficult to dissolve is the one which precipitates or separates when solutions of each solute in the same solvent are poured together.

Dissolving two or more polymers in the same solvent may not solve the problem of producing a good film after solvent evaporation. Here again the best chances for film formation will be found when the solvent is chosen as described for dissolving the polymers. A film can be formed from a solution with a good solvent when it may not be possible to do so with a poorer solvent. Film formation becomes more difficult as the number of high polymer components increases. Care must also be taken if solvent mixtures are used. In this case one of the components may evaporate first leaving a non-solvent behind. Film formation is essentially a problem of maintaining solubility until the film has attained a certain rigidity. Since the polymer concentration increases during the evaporation process, a solvent quality is sometimes necessary which is better than that required just to dissolve the polymers (G).

The principles outlined here can be used in reverse if application to a polymer substrate is required. Choosing the solvent outside of the volume of solubility of the substrate, or at least such that it contains poor solvents for the substrate, should help to avoid the problem of dissolving the substrate.

## 4.6 *Plasticizers*

No special studies of plasticizer compatibility in relation to plasticizer locations in the system have been performed. It would be logical to assume that the closer the plasticizer lies to the center of the volume of solubility of a polymer, the more compatible it will be with the given polymer.

Plasticizers dissolve many polymers and resins. In many cases non-dissolving plasticizers have been combined with non-dissolving solvents to give a mixture which dissolves a given solute. In an extreme case involving dimethyl phthalate and propylene glycol such a combination of a non-dissolving plasticizer and a non-solvent showed immiscibility when equal volumes were combined. When the intended solute, P, was added to his two phase system, the whole mixture yielded a clear solution. This should emphatically demonstrate the need to include plasticizers in any estimation of the solubility parameters of mixtures if there are significant quantitites present.

Table 4.2
List of Pigments Studied

| Pigment | Description |
|---|---|
| 1 | $TiO_2$, *Kronos RN 57*, Titan Co. A/S., Frederikstad, Norway. |
| 2 | *Phthalocyanine Blue*, B6, E. I. du Pont de Nemours and Co. (1949). |
| 3 | *Isolbonared Nr. 7522, C. I. Pigment Red 48* (C.I. 15865) (MnSalt), Køge Chemical Works, Køge, Denmark. |
| 4 | *Peerless Carbon Black* |
| 5 | *Isol Fast Yellow 10 GX 2505, C.I. Pigment Yellow 3*, Køge Chemical Works, Køge, Denmark. |
| 6 | *Reflex Blau TBK Ext.* (No C.I. Index-pigment mixture), Farbwerke Hoechst, Frankfurt (M), West Germany. |
| 7 | *Isol Ruby BKS 7520, C.I. Pigment Red 57* (C.I. 15850) (Ca Salt), Køge Chemical Works, Køge, Denmark. |
| 8 | *Hansagelb 10 G, C.I. Pigment Yellow 3* (C.I. 11710), Farbwerke Hoechst, Frankfurt (M), West Germany. |
| 9 | *Fanalrosa G Supra Pulver, Pigment Red 81* (C.I. 45160), BASF, Ludwigshafen, West Germany. |
| 10 | *Heliogenblau B Pulver, C.I. Pigment Blue 15* (C.I. 74160), BASF, Ludwigshafen, West Germany. |
| 11 | *Heliogengrün GN, C.I. Pigment Green 7*, (C.I. 74260), BASF, Ludwigshafen, West Germany. |
| 12 | *Permanentgelb H 10 G, C.I. Pigment Yellow 81*, (No C.I. index), Farbwerke Hoechst, Frankfurt (M), West Germany. |
| 13 | *Permanent Bordeaux FRR, C.I. Pigment Red 12* (C.I. 12385), Farbwerke Hoechst, Frankfurt (M), West Germany. |
| 14 | *Permanent Violet RL Supra, C.I. Pigment Violet 23*, (C.I. 12505), Farbwerke Hoechst, Frankfurt (M), West Germany. |
| 15 | *Isol Benzidine Yellow G 2537, C.I. Pigment Yellow 12* (C.I. 21090), Køge Chemical Works, Køge, Denmark. |
| 16 | *Brillfast Sky Blue 3862, C.I. Pigment Blue 3* (C.I. 42140), J. W. and T. A. Smith Ltd., London, Great Britain. |
| 17 | *Permanent Orange G, C.I. Pigment Orange 13* (C.I. 21110), Farbwerke Hoechst, Frankfurt (M), West Germany. |
| 18 | *Permanent Red, FGR Extra Pulver, C.I. Pigment Red 112*, (C.I. 12370). Farbwerke Hoechst, Frankfurt (M), West Germany. |
| 19 | *Isol Fast Red 2G 2516, C.I. Pigment Orange 5*, (C.I. 12075), Køge Chemical Works, Køge, Denmark. |
| 20 | *Monolite Fast Blue 3 RS, Powder, C.I. Vat Blue 4* (C.I. 69801), Imperial Chemical Industries. |
| 21 | *Heliogenblau LG, Pulver, C.I. Pigment Blue 16* (C.I. 74100), BASF., Ludwigshafen, West Germany. |
| 22 | *Red Iron Oxide.* |
| 23 | *Carbon Black, Printex V* (5519–1), Degussa, Frankfurt (M), West Germany. |
| 24 | *Aluminium Pulver Lack 80*, Eckart-Werke, 851 Fürth/Bayern, West Germany. |
| 25 | *Isol Benzidene Yellow GA-PR, 9500, C.I. Pigment Yellow 12*, Køge Chemical Works, Køge, Denmark. (See Figures 4.10, 4.11 and 4.12). |

Table 4.3
Characteristic Parameters for Various Pigments

| Pigment | $\delta'_o$ | $\delta'_{do}$ | $\delta'_{po}$ | $\delta'_{ho}$ | $\delta'_{ao}$ | $R'_{Ao}$ | Comments |
|---|---|---|---|---|---|---|---|
| 1 | 16.8 | 11.8 | 7.3 | 9.5 | 12.0 | 8.4 | Suspension |
| 2 | 10.5 | 9.3 | 3.1 | 3.7 | 4.8 | 2.3 | Few suspending solvents |
| 3 | 10.0 | 8.7 | 3.5 | 3.5 | 5.0 | 2.5 | Few suspending solvents |
| 4 | 13.6 | 10.3 | 6.0 | 6.6 | 8.9 | 6.0 | Suspension |
| 5 | 11.9 | 10.2 | 4.8 | 3.8 | 6.1 | 4.4 | Color only |
| 6 | 13.2 | 10.8 | 3.8 | 6.6 | 7.6 | 7.0 | Mixed color and suspension |
| 7 | 10.5 | 9.6 | 3.0 | 3.2 | 4.4 | 3.9 | Suspension |
| 8 | 10.5 | 9.1 | 4.0 | 3.3 | 5.2 | 3.3 | Color only |
| 9 | 13.0 | 9.8 | 7.0 | 5.0 | 8.6 | 5.2 | Color only |
| 10 | 12.0 | 10.8 | 3.5 | 4.0 | 5.3 | 5.2 | Suspension |
| 11 | 12.0 | 10.0 | 4.8 | 4.5 | 6.6 | 4.8 | Primarily suspension |
| 12 | 8.8 | 8.4 | 1.5 | 2.3 | 2.7 | 2.2 | Suspension |
| 13 | 13.2 | 10.7 | 4.8 | 6.1 | 7.8 | 5.2 | Color only |
| 14 | 11.5 | 9.6 | 5.2 | 3.6 | 6.3 | 4.4 | Mixed color and suspension |
| 15 | 10.2 | 9.3 | 3.0 | 2.9 | 4.2 | 3.9 | Mixed color and suspension |
| 16 | 13.3 | 9.5 | 7.2 | 6.0 | 9.4 | 5.1 | Suspension |
| 17 | 11.5 | 9.7 | 3.9 | 4.7 | 6.1 | 4.5 | Color only |
| 18 | 11.2 | 10.0 | 3.5 | 3.5 | 5.0 | 5.0 | Color only |
| 19 | 14.2 | 10.9 | 5.6 | 7.1 | 9.0 | 7.0 | Primarily color |
| 20 | 15.2 | 10.8 | 6.5 | 8.5 | 10.7 | 7.0 | Suspension |
| 21 | 13.5 | 10.7 | 5.0 | 6.5 | 8.2 | 6.0 | Suspension |
| 22 | 13.7 | 10.1 | 6.0 | 7.0 | 9.2 | 5.6 | Suspension |
| 23 | 13.1 | 10.3 | 6.0 | 5.5 | 8.1 | 5.5 | Suspension |
| 24 | 10.4 | 9.3 | 3.0 | 3.5 | 4.6 | 2.4 | Suspension |
| 25 | 9.1 | 9.0 | 2.7 | 2.3 | 3.6 | 2.5 | Suspension |

### 4.7 *Non-ionic Emulsifiers*

No special studies on the emulsifying properties of the non-ionic emulsifiers have been conducted to relate their solubility parameter characterization to their practical properties. It would seem reasonable that this could be done.

### 4.8 *Dyes*

Dyes have volumes of solubility. These volumes will be smaller for higher dye solubilities. The concept of improving solvent quality can be used to improve dye solubility in cases where this is desired.

### 4.9 *Pigment-Binder-Solvent Interactions*

The pigments listed in Table 4.2 have been characterized by the values given in Table 4.3. The ability to characterize binders and pigments through their interactions with a series of well-defined solvents should lead to more systematic paint

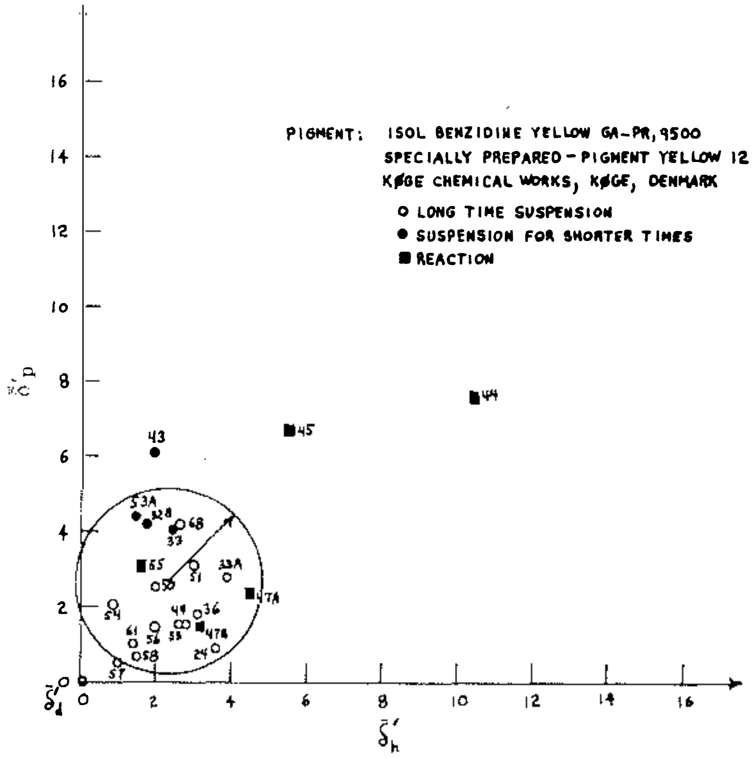


Figure 4.10. The volume of suspension for a pigment. (Primes are used to distinguish surface properties)

and printing ink formulation. What is generally wanted in pigmented systems is binder adsorption onto the pigment. Returning to the principle that materials with similar solubility parameters attract each other, one concludes that when the binder and pigment volumes of interaction overlap, there will be good interaction between them; binder should adsorb on the pigment. Furthermore, the solvent should not adsorb on the pigment, so its placement in the system should not be such as to interfere with pigment-binder interactions. Thus, the ideal is evidently to have a reasonably good solvent for the binder, with the binder center placed between the solvent point and the pigment center. A reasonably large overlap in the volumes of interaction for the pigment and the binder would also be desirable. Schaeffer (1965) has discussed the importance of the nature of binder adsorption.

Various experiments to clarify these phenomena have been performed by the technical staff at Køge Chemical Works and by Mr. Skaarup in these laboratories. These experiments are not completed, but the general picture to be gotten from the existing data is that the generalities listed above seem to hold. It may be

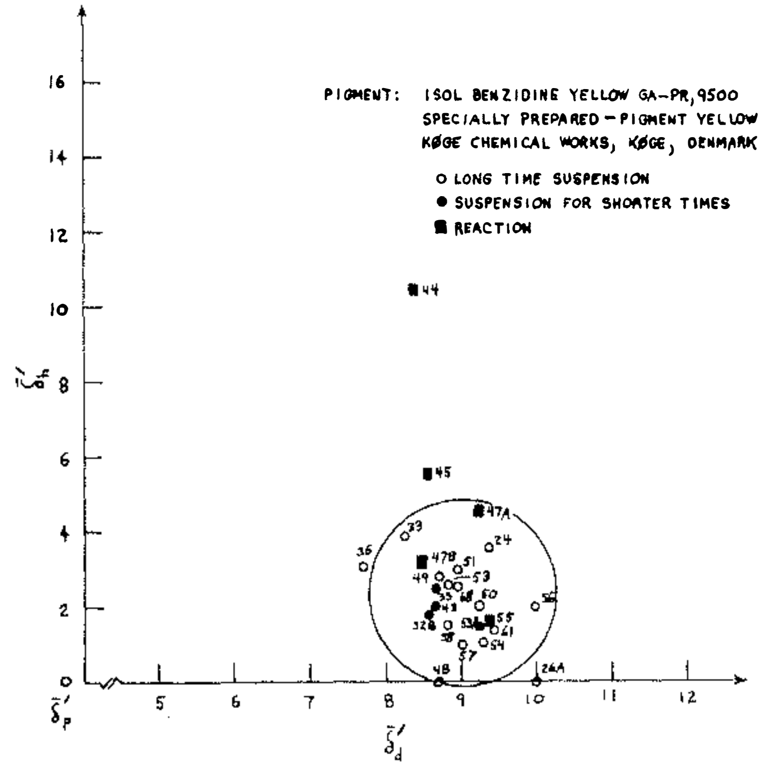


Figure 4.11. The volume of suspension for a pigment. (Primes are used to distinguish surface properties)

possible to allow some flocculation of both pigments in two pigment systems; apparently the pigments must behave similarly (Vinther 1965, Petersen 1966).

Sørensen (1967) has discussed the application of the solubility parameter to printing ink formulation. The minima in the reported viscosity curves are found when the binder center lies between the solvent and the pigment center as described above. The minima are located in the center of the volume of solubility for the given binder in unpigmented systems; they are located on the opposite side of this center from the pigment when it is added. These minima are associated with good print quality. This relative placement of pigment and binder is not sufficient to explain all the results, however. An increase in the apparent adsorption activity of the pigment evidently leads to greater binder adsorption and a reduction of the absolute viscosity. An increase in the apparent adsorption activity is reflected by an increase in the number of long time suspending solvents in suspension testing. Both the placement of the pigment in the solubility parameter system as well as the intensity of the interaction possible in this placement (apparent adsorption activity) affect pigment-binder interactions. The nature of the active

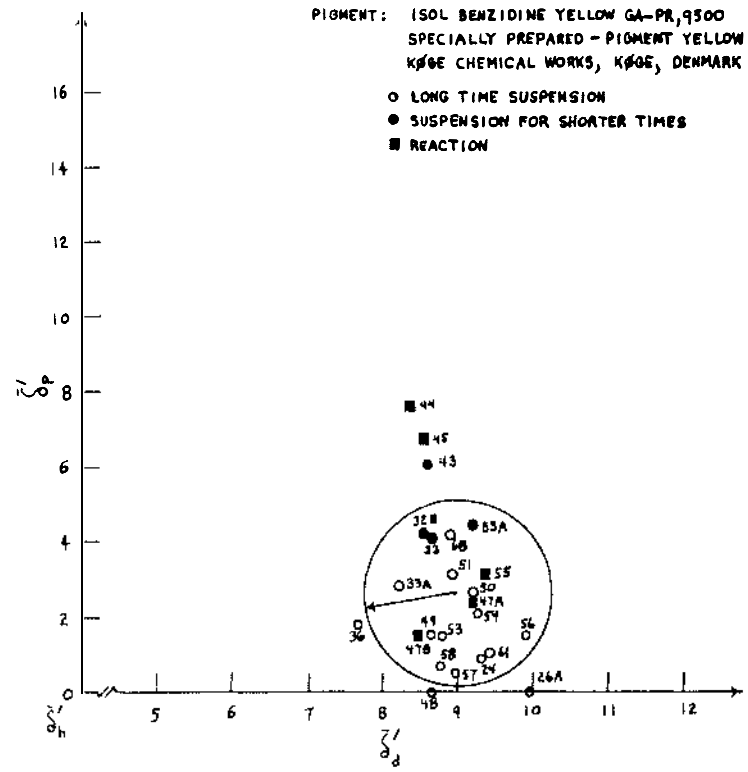


Figure 4.12. The volume of suspension for a pigment. (Primes are used to distinguish surface properties)

pigment surface determines the nature of the interaction. Much more work is necessary to fully clarify the effects described in this section.

To assist in the characterization of pigment surfaces, viscosity and density data for the solvents have been included in Appendix A.3. The volumes of suspension for a pigment are given in Figures 4.10, 4.11, and 4.12.

## 4.10 *Conclusion*

The three dimensional solubility parameter can be used to characterize many materials and to infer interactions among them. Numerous examples have been given to demonstrate this and to provide a guide for using the system effectively. This concept can unquestionably be used to gain insight into numerous other phenomena and problems not discussed here. The basic means of characterization by interactions with a set of well-defined solvents will remain essentially the same regardless of the material to be characterized.

The term solubility parameter does not adequately represent the predictive possibilities of the system, particularly where a solid surface is involved. Terminology to include these situations should be adopted, with the term attraction being incorporated in some manner.

*Chapter 5*

# The Process of Solvent Evaporation

## 5.1 *Introduction*

The purpose of this section is to demonstrate how the division of the process of solvent evaporation into two distinct phases (A, B, C) can be used to solve practical problems in film drying.

Use of the solubility parameter concept allows selection of all possible combinations of solvents to help solve such problems, and consideration of the solvent molecular geometry allows rapid estimation of which solvents will diffuse more rapidly from the film. Smaller, linear molecules diffuse more rapidly through the type polymer films normally used in the paint and varnish industry. It does not matter whether they are alcohols, polar solvents, or those generally considered non-hydrogen bonding.

A mathematical description of the process of solvent evaporation as described in this chapter is included in Chapter 7.

## 5.2 *The Two Phases of Solvent Evaporation*

The loss of solvent from a polymer film occurs in two distinct phases. The first of these is controlled by boundary layer resistance to solvent transport, and the second is controlled by internal diffusion resistance to solvent loss. This two stage drying can be seen in Figures 5.1 and 5.2. The sharp downward trend at short times is the first stage, and the long flat portion of the curve which extends to an indefinitely long time is the second stage.

Time, t, divided by dry film thickness, L′, has been used for Figure 5.1, rather than time alone, to demonstrate that boundary layer resistance to solvent loss controls solvent evaporation. Plotting in this manner collects the curves for various film thicknesses in the first stage. This is equivalent to saying that doubling the film thickness also doubles the drying time in the first stage, since the amount of solvent initially applied has also been doubled. Drying time to the break in the curve is directly related to the evaporation ratio reported by Doolittle (1954).

Diffusion theory predicts solvent loss should be dependent on the square of the dry film thickness, which is shown to be the case in the second phase in Figure 5.2. Here boundary layer resistance is negligible. Drying curves of the type shown in this figure have been calculated on the basis of the diffusion theory described in Chapters 6 and 7. Since the break in the curve at the change over

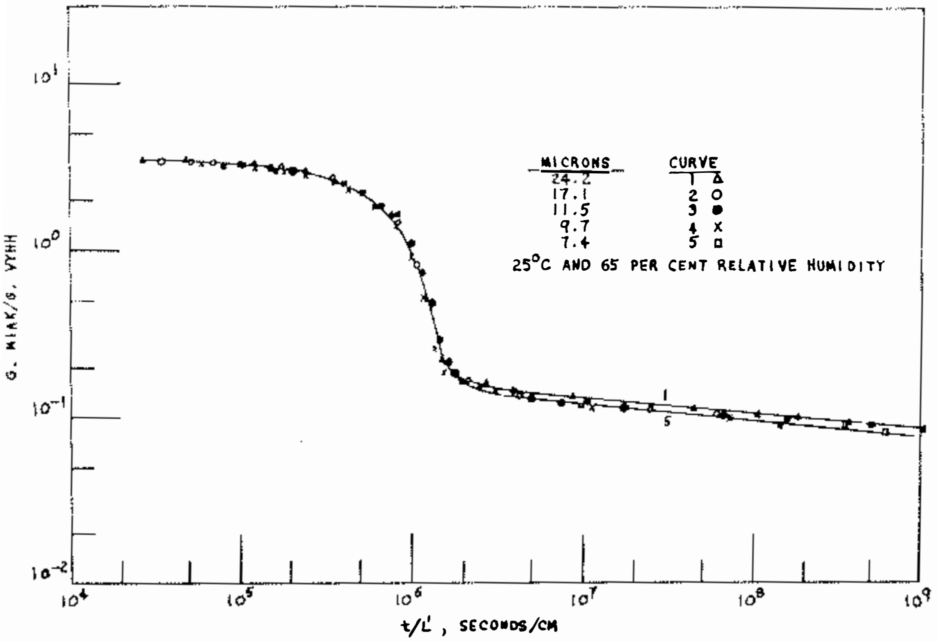


Figure 5.1. Drying data for methyl isoamyl ketone in Vinylite® VYHH, t/L′ as abscissa

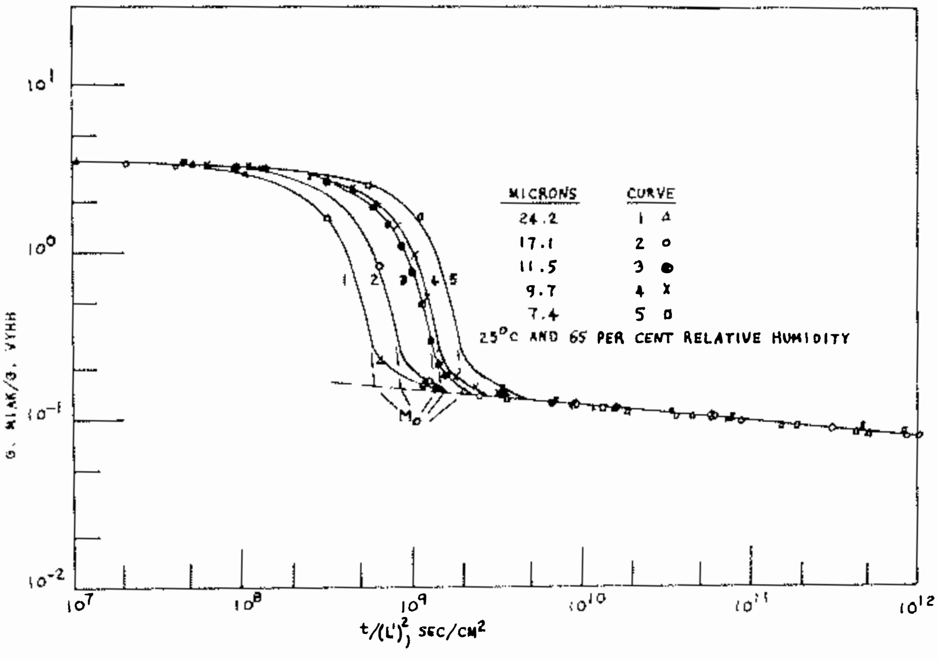


Figure 5.2. Drying data for methyl isoamyl ketone in Vinylite® VYHH, t/L′$^2$ as abscissa

from the first phase to the second phase does not indicate a thoroughly dry film, attention has been given to the second phase of drying. Solvent contained in the film beyond this point is considered retained solvent.

One day after application a typical film of 30 microns thickness will be located at a $t/(L')^2$ of $9.6 \times (10)^9$ sec/cm² on the type plot shown in Figure 5.2.

## 5.3 *Why is Solvent Retained?*

Solvent is retained in high polymer films because it can not diffuse rapidly through the polymer matrix. Mathematically one would say the solvent has a low diffusion coefficient in the polymer. The result of a low diffusion coefficient is that the solvent is held or retained in the film, perhaps for many years. It is not held by hydrogen or polar bonds, it quite simply has trouble finding anywhere to move to in the rather dense network of polymer chain segments surrounding it. Moving all of these chain segments, and their neighbors again, so that a solvent molecule can find enough space to move requires a lot of energy. The activation energy for this process may well be 30–40 Kcal/mole in poly(vinyl acetate) (Kokes and Long 1953), a value considerably higher than hydrogen or polar bonding energies. Hydrogen and polar bonding energies are somewhat less than the energy of evaporation of the solvent.

## 5.4 *The Effect of Various Factors on Solvent Retention*

Once it is realized that it is polymer chain segment mobility and the difficulty of finding a place to move to which retains solvent in a polymer film, the effect of numerous of the factors affecting solvent retention can be explained (A, B, C). The rate of loss, indicated by the slope of the second phase curve in Figure 5.2, is increased with increasing mobility within the film at the prevailing temperature. The ratio of the amount of solvent to the amount of dry polymer at the beginning of the second phase, $M_0$, is directly related to the reduction of the glass transition temperature, $T_g$, by the presence of solvent.

$T_g$ is a measure of the mobility of the polymer chain segments since it is that temperature at which groups attached to the polymer backbone can just begin to rotate about the axis of the backbone. The $T_g$ of the film must evidently be close to room temperature or higher for significant solvent retention to occur. $T_g$ is higher for higher frequencies of testing.

The presence of plasticizer or an increase in temperature gives the polymer chain segments more mobility. $M_0$ is decreased and the rate of loss increases in both cases. Less solvent is required to reduce the $T_g$ of the film to a given value than had the plasticizer been absent or the temperature lower; both solvent and plasticizer reduce $T_g$. A decrease in the molecular weight of the polymer can also lead to less solvent retention if the $T_g$ of the polymer is decreased.

Increasing the velocity of air past the surface of a drying film decreases the boundary layer resistance relative to internal diffusion resistance. The first phase evaporation is more rapid, but $M_0$ is increased and slightly more solvent will be held in the film in the second phase if the air velocity is high (Jülke 1962). The calculations reported in Figure 7.4 demonstrate that changing boundary layer resistance relative to internal diffusion resistance is not, in itself, sufficient to explain this increase of $M_0$. Cooling of the film to a point closer the break in the drying curve is thought significant in this case. This cooling during solvent evaporation would hinder internal diffusion and lead to a greater $M_0$, since the film enters the second phase at a lower temperature.

The presence of moderate amounts of pigment increases $M_0$ and slows diffusion in the second phase. The pigment particles increase the average path length to the surface increasing internal diffusion resistance for a given film thickness. $M_0$ is calculated from the mass and volume of the polymer and not the entire film, for this case. Some excess solvent is more or less trapped in the film at the end of the first phase by the pigment particles since it can not get to the surface rapidly enough to escape before the outer film layer retards solvent loss by internal diffusion.

The absorption of water affects solvent evaporation by plasticizing the film and enabling a more rapid loss of solvent.

### 5.5 *The Plasticizing Effectiveness of Solvents*

Torsion pendulum studies of the effect of solvent in polymer films demonstrate that solvents have a stronger plasticizing action than plasticizers. If one measures the damping of torsional oscillations of a sample at about 1 c/s as a function of temperature, a maximum is found at a temperature, $T_d$, about 15 degrees higher than the $T_g$ found from volume expansion measurements. This temperature has been measured for dry polymer films as well as for films of the same polymers containing solvent or plasticizers by a technique described earlier (B, C).

Plasticizing effectiveness is defined as the decrease in the temperature of the damping maximum divided by the volume fraction of diluent present, $v_f$.

$$\text{5.1)} \qquad \text{P.E.} = \frac{T_{d_p} - T_{d_{s,p}}}{v_f}$$

with $v_f$ calculated from

$$\text{5.2)} \qquad v_f = \frac{\dfrac{M_s}{M_p}\,\dfrac{\rho_p}{\rho_s}}{1 + \dfrac{M_s}{M_p}\,\dfrac{\rho_p}{\rho_s}}$$

Table 5.1
The Plastizing Effectiveness of Diluents in Various Polymers

| Diluent | $V_m$ | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|---|---|
| $H_2O$ | 18 | – | – | – | – | 705 | – | – |
| Methanol | 40.7 | – | – | – | 432 | 570 | – | – |
| Carbon disulfide | 60.6 | – | – | – | – | – | 674 | – |
| Acetone | 74.0 | – | – | – | – | – | – | 353 |
| Dimethyl formamide | 77.0 | 374 | 294 | – | – | – | – | – |
| Ethylene chloride | 79.4 | – | – | – | – | – | 483 | – |
| Methyl acetate | 79.7 | – | – | – | – | – | 512 | 417 |
| Pyridine | 80.4 | 295 | – | – | – | – | – | – |
| Chloroform | 80.7 | – | – | – | – | – | 485 | 214 |
| Dioxane | 85.7 | 257 | 313 | 341 | – | – | – | – |
| 1,2 Dibromoethane | 86.2 | 319 | 290 | 373 | – | – | – | – |
| 2-Nitropropane | 86.9 | 303 | 270 | 336 | – | – | – | – |
| Methylal | 88.8 | – | 263 | – | – | – | – | – |
| l-Nitropropane | 89.0 | 310 | – | – | – | – | – | – |
| Benzene | 89.4 | – | 246 | – | 250 | – | 351 | 248 |
| Methyl ethyl ketone | 90.2 | 329 | 334 | 443 | 270 | – | – | – |
| Trichloroethylene | 90.2 | 314 | 259 | 353 | – | – | – | – |
| Aniline | 91.1 | 324 | 260 | 386 | – | – | – | – |
| Butanol | 91.8 | – | – | – | – | – | – | 265 |
| Carbon tetrachloride | 97.1 | – | 203 | – | – | – | 426 | – |
| 1-Iodopropane | 98.3 | – | – | – | 234 | – | – | – |
| Ethyl acetate | 98.5 | 308 | 320 | 428 | 287 | – | 497 | 374 |
| 2-Iodopropane | 100 | – | – | – | 231 | – | – | – |
| Chlorobenzene | 102.1 | 275 | 317 | – | 247 | 200 | – | – |
| Nitrobenzene | 102.3 | – | 265 | 298 | – | – | 386 | 294 |
| Cyclohexanone | 104.0 | 228 | 330 | 278 | – | – | – | – |
| Toluene | 106.4 | 293 | 293 | – | – | – | 346 | 235 |
| Mesityl oxide | 115.6 | – | 214 | – | – | – | – | – |
| Propyl acetate | 115.7 | – | – | – | – | – | – | 369 |
| Diacetone alcohol | 124.2 | 250 | – | 321 | – | – | – | – |
| Methyl isobutyl ketone | 125.8 | 313 | 273 | 359 | 244 | – | – | – |
| Methyl salicylate | 129.0 | – | – | – | – | – | 395 | – |
| 2-Butoxy ethanol | 132.0 | – | 223 | – | – | – | – | – |
| n-Butylacetate | 132.5 | 259 | 282 | 423 | – | – | 378 | 366 |
| Cellulose acetate | 136.2 | 240 | 244 | 362 | – | – | – | – |
| Methyl isoamyl ketone | 142.8 | 278 | – | – | – | – | – | – |
| Tetralin | 152 | – | 227 | – | – | – | – | – |
| Phenyl salicylate | 171.5 | – | – | – | – | – | 333 | – |
| β-naphthyl salicylate | 214 | – | – | – | – | – | – | 257 |
| Dibutyl phthalate | 265 | 198 | 220 | – | 228 | 115 | – | – |
| Tricresyl phosphate | 337 | – | – | – | – | – | 316 | – |
| Dioctyl phthalate | 396 | 175 | – | – | – | 113 | – | – |
| Citroflex A-8 | 571 | 164 | 219 | – | 174 | – | – | – |
| Paraplex G-50 | 2040 | 161 | – | – | – | – | – | – |
| Paraplex G-25 | 7540 | 145 | – | – | – | – | – | – |

Polymers:
1. Vinylite® VYHH, vinyl chloride-vinyl acetate copolymer, $T_d = 79°$
2. PEMA-poly (ethyl methacrylate), $T_d = 86°$
3. Epikote® OL 55-epoxy, $T_d = 104°$
4. Butvar® B-76-poly (vinyl butyral), $T_d = 77.5°$
5. Mowilith®-50-poly (vinyl acetate), $T_d = 47°$
6. Poly (styrene)-(Dimarzio and Gibbs 1963) (data from (Jenkel and Heusch 1953)
7. Poly (methyl methacrylate)- (data from ibid.)

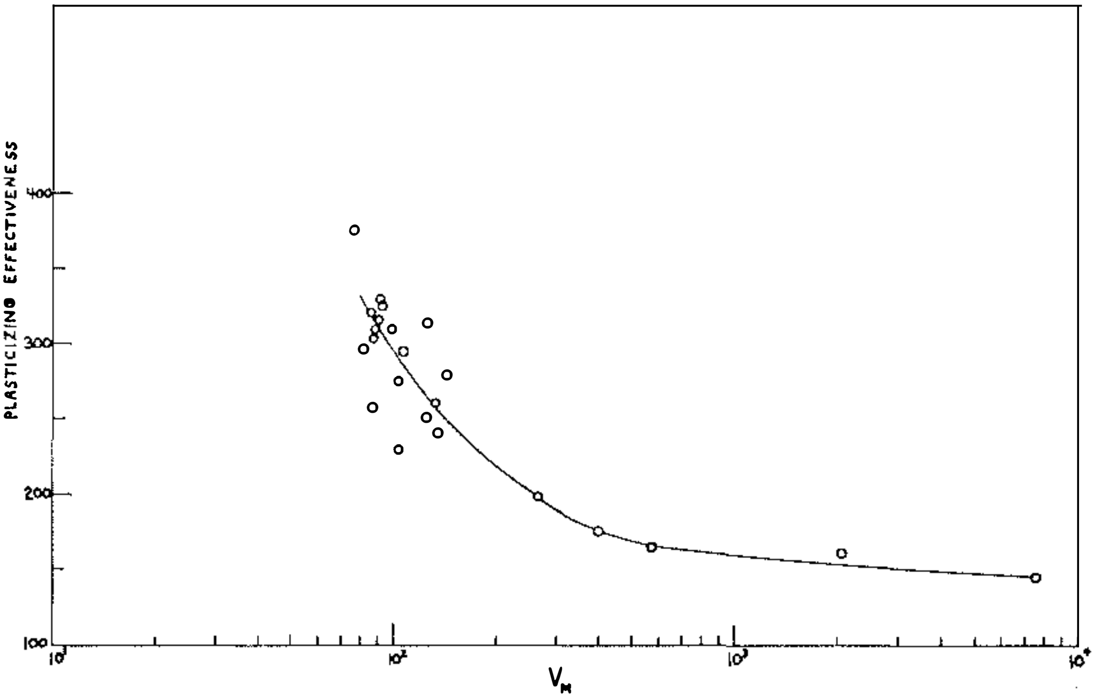


Figure 5.3. The plasticizing effectiveness of various diluents in Vinylite VYHH

Here:

$T_{d_p}$ = $T_d$ of pure polymer
$T_{d_{s,p}}$ = $T_d$ of polymer with diluent
$M_s$ = mass of diluent present
$M_p$ = mass of polymer present
$\rho_p$ = density of polymer
$\rho_s$ = density of diluent

Data for the plasticizing effectiveness of various diluents in polymers are included in Tables 5.1 and 5.3. In spite of the fact that a log-log or semilog plot of plasticizing effectiveness versus diluent $V_m$ has a tendency to curve upwards at low $V_m$ in some cases, a statistical treatment of the data assuming a straight line on this plot was performed. The intended purpose of this treatment was to demonstrate that diluents of low $V_m$ (solvents) tended to be more effective plasticizers than those of high $V_m$ (plasticizers). Thus the slopes of plots similar to Figure 5.3 are negative for poly(vinyl butyral), poly(styrene), poly(vinyl acetate), and Vinylite® VYHH. These slopes are inconclusive for Epikote OL-55, poly(methyl methacrylate), and poly(ethyl methacrylate). This is taken as confirmation of the desired generalization which is, moreover, expected (B, Dimarzio and Gibbs 1963).

Table 5.2
The Temperature of the Damping Maximum at Frequencies Near 1 c/s and the König Pendulum Hardness for Commercially Available Varnishes and Lacquers

| Coating | Thickness microns | Days aging | $T_d$ | Pendulum hardness |
|---|---|---|---|---|
| 1. Urethane, oleoresinous | 36 | 7 | 32 | 24 |
| | | 28 | 32 | 27 |
| 2. Epoxy ester | 38 | 7 | 27 | 36 |
| | | 28 | 35 | 60 |
| 3. Poly (vinyl acetate) | 33 | 7 | 25 | 38 |
| | | 28 | 28 | 64 |
| 4. Oleoresinous | 27 | 7 | 30 | 55 |
| | | 28 | 39 | 75 |
| 5. Chlorinated Rubber A | 34 | 7 | 46 | 91 |
| | | 28 | 55 | 100 |
| B | 63 | 7 | 43 | 53 |
| | | 28 | 49 | 68 |
| 6. Acid hardening, Urea Formaldehyde-Poly (vinyl butyral) | 27 | 7 | 53 | 140 |
| | | 28 | 56 | 164 |
| 7 2 Component isocyanate | 23 | 7 | 70 | 178 |
| | | 28 | 70 | 180 |
| 8 Amide hardened epoxy | 25 | 7 | 52 | 183 |
| | | 28 | 57 | 189 |
| 9. Amine hardened epoxy | 30 | 7 | 49 | 185 |
| | | 28 | 54 | 191 |
| 10. Stoving acrylic | 60 | 7 | 87 | 203 |
| | | 28 | 88 | 210 |

Note: Higher hardness numbers indicate harder films.

The plasticizing effectiveness of the solvents is apparently independent of chemical composition, but not of molecular geometry. The concept of anti-plasticizers has been discussed in the recent literature (Jackson and Caldwell 1965, 1966). These are reported as being effective in polymers having stiff chains with rigid groups, and are themselves stiff molecules with polar groups having at least two non-bridged rings, glass transition temperatures greater than —50°, and one dimension less than about 5.5Å in at least 65% of the molecule. These decrease the $T_g$ of the polymer, though somewhat less than normal plasticizers, and within a rather large concentration range increase the tensile modulus and tensile strength while decreasing elongation. Thus flatly saying that a decrease in $T_g$ leads to plasticizing is not precise. To help demonstrate the ability of $T_d$ to describe common coating materials, the data given in Table 5.2 and Figure 5.4 have been accumulated.

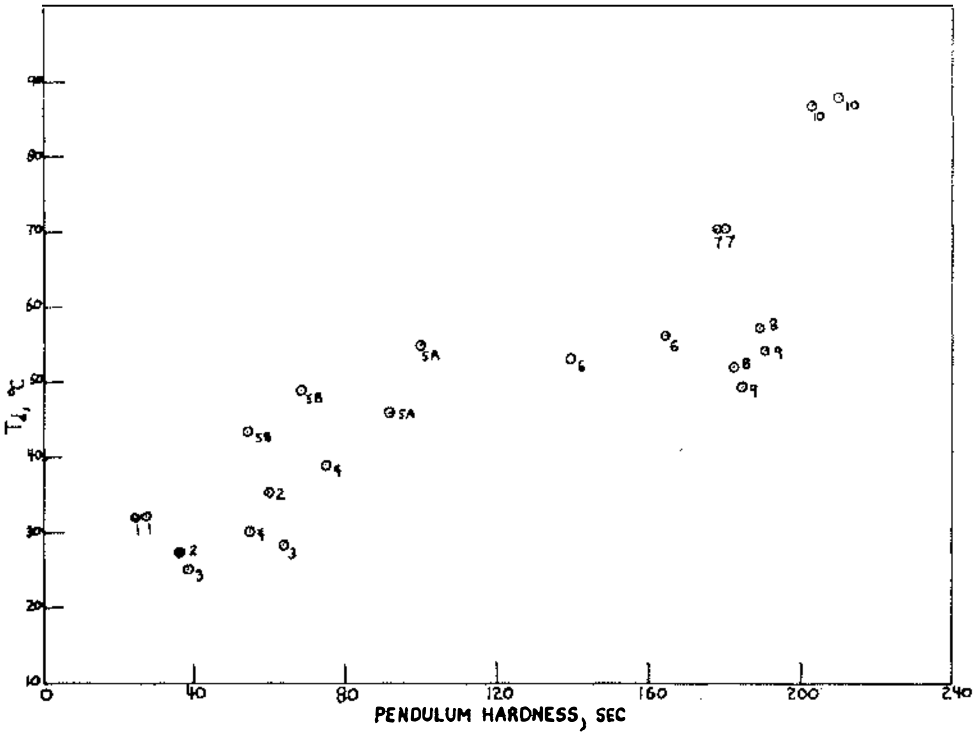


Figure 5.4. $T_d$ versus König pendulum hardness for some commercially available surface coatings

The general effect of plasticizers in coatings has been discussed (D, Doolittle 1954, Mellan 1961, Mellan 1963). The effect of solvent will be essentially the same as that of plasticizer, with the added restriction that the solvent will not be evenly distributed in the film. There will be more at the substrate than close to the film surface, assuming, of course, that the substrate does not absorb solvent. See Chapter 7.

The general tendency of the results measured with the torsion pendulum also demonstrates a lower plasticizing effectiveness for rigid, cyclic molecules compared to flexible, linear molecules. Typical data are plotted in Figure 5.3 for the plasticizing effectiveness of numerous diluents in Vinylite VYHH. Dioxane and cyclohexanone stand out for their low values. The data on VYHH is considered the most reliable since the effect of the concentration gradient in these films is thought less in this case due to their greater solvent retention. The concentration gradients to be expected in drying films have been calculated on the basis of the mathematics given in the following chapters.

To avoid evaporation of the diluent, the closed apparatus sketched in Figure 5.5 was used to study the effect of water and methanol on poly(vinyl acetate) and the

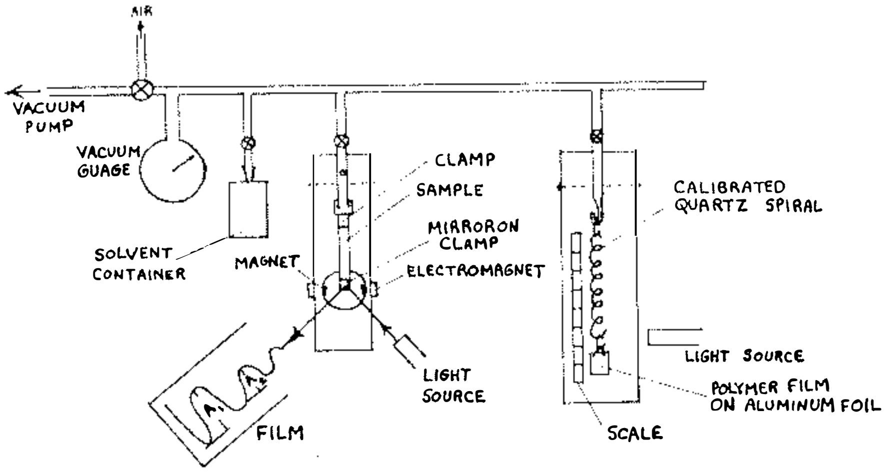


Figure 5.5. Sketch of closed torsion pendulum and diffusion apparatus

Table 5.3
Damping Data for Diluents with Low Molar Volumes

| Polymer | Diluent | $v_f$ | $T_{d_g,p}$ | Effectiveness | Molar volume |
|---|---|---|---|---|---|
| Poly (vinyl acetate)........... | Water......... | .031 | 25.4 | 705 | 18 |
|  | Methanol...... | .039 | 25.0 | 570 | 40.7 |
| Poly (vinyl butyral)........... | Methanol...... | .134 | 19.5 | 432 | 40.7 |

effect of methanol on poly(vinyl butyral). Data for these particular cases are given in Table 5.3 to emphasize how much a small amount of these diluents can do. For these measurements the temperature of the surroundings was raised while keeping the pressure such that the extension of the calibrated quartz spiral was essentially constant. Solvent content was calculated from the extension of the spiral, and the damping, Λ, was measured as the natural logarithm of the ratio of the amplitudes of successive oscillations. A film recorded the light reflected from the oscillating sample. Excitation of the torsional oscillations was done by an electromagnet. This same apparatus was used for measuring diffusion coefficients as described in the next chapter.

## 5.6 *How to Reduce Solvent Retention*

Data on the retention of the solvents shown in Figure 5.10 are given in Figures 5.6, 5.7, 5.8, and 5.9. The principle involved in reducing solvent retention becomes

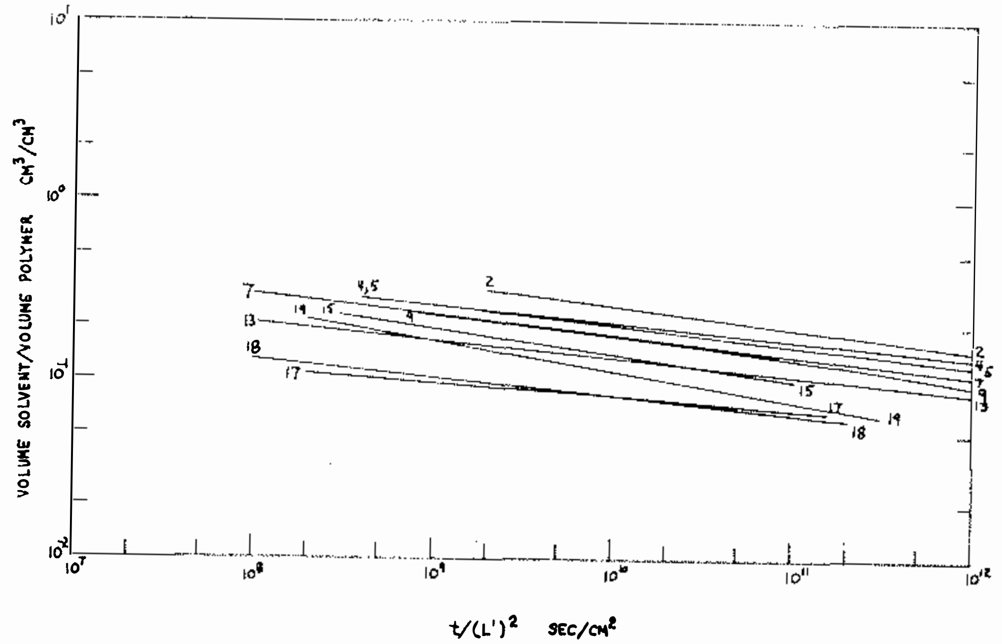


Figure 5.6. Retention of solvents in Vinylite VYHH, 25°C and 65 per cent relative humidity (Key to numbers in Figure 5.10)

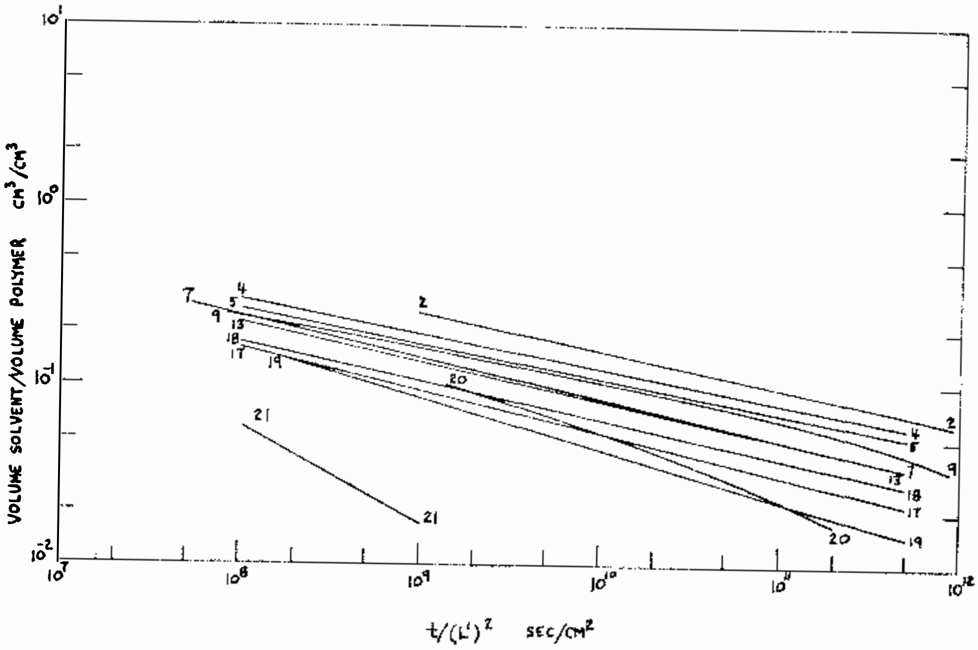


Figure 5.7. Retention of solvents in poly(vinyl acetate), 25°C and 65 per cent relative humidity (Key to numbers in Figure 5.10)

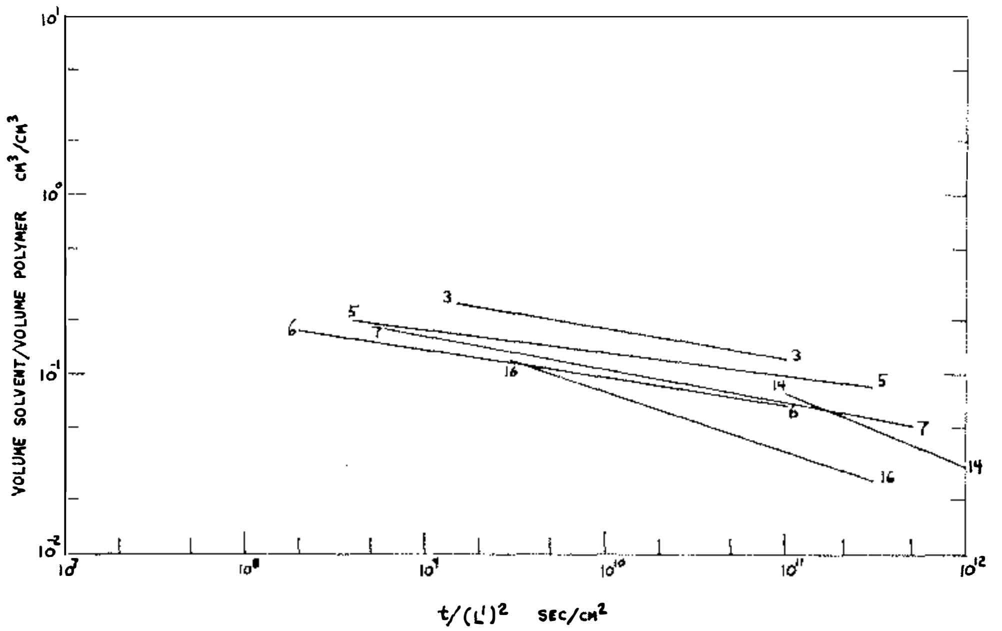


Figure 5.8. Retention of solvents in poly(ethyl methacrylate), 25°C and 65 per cent relative humidity (Key to numbers in Figure 5.10)

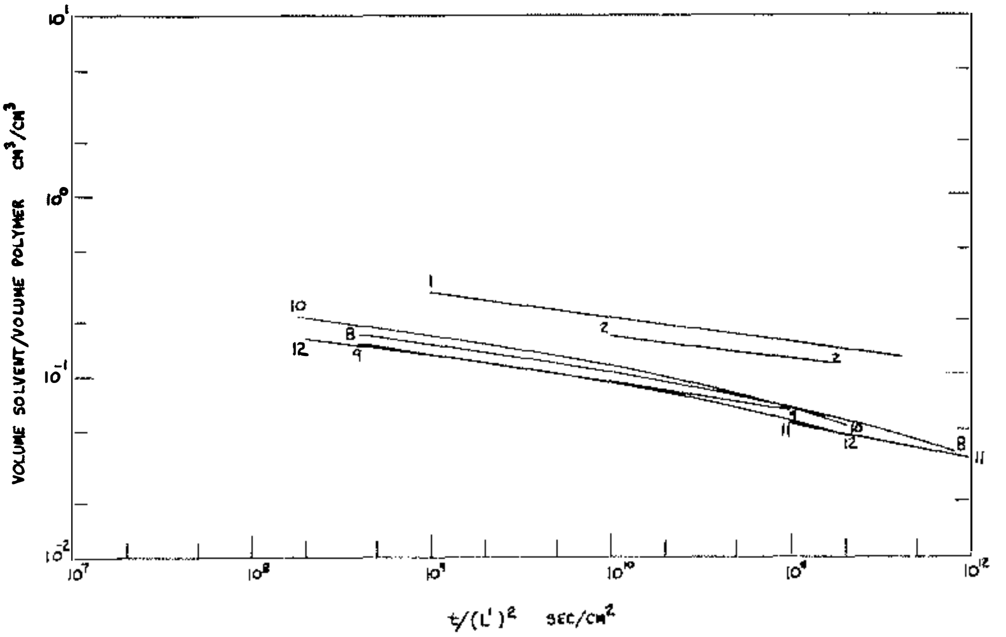
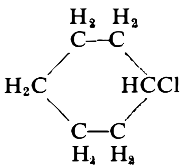
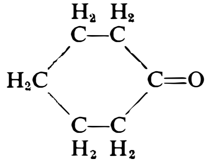
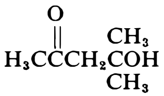


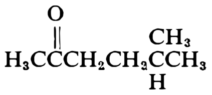
Figure 5.9. Retention of solvents in poly(ethyl methacrylate), 25°C and 65 per cent relative humidity (Key to numbers in Figure 5.10)

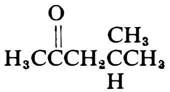
Figure 5.10. Approximate Order of Retention of Solvents in Polymer Films

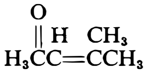
1. CYCLO HEXYL CHLORIDE


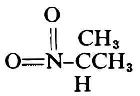
2. CYCLOHEXANONE


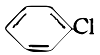
3. DIACETONE ALCOHOL

$H_3C\overset{\overset{O}{\|}}{C}CH_2\overset{CH_3}{\underset{CH_3}{C}}OH$

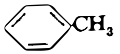
4. METHYL ISOAMYL KETONE

$H_3C\overset{\overset{O}{\|}}{C}CH_2CH_2\overset{CH_3}{\underset{H}{C}}CH_3$

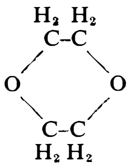
5. METHYL ISOBUTYL KETONE

$H_3C\overset{\overset{O}{\|}}{C}CH_2\overset{CH_3}{\underset{H}{C}}CH_3$

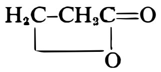
6. MESITYL OXIDE

$H_3C\overset{\overset{O}{\|}}{C}\overset{H}{C}{=}\overset{CH_3}{C}CH_3$

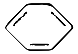
7. 2-NITRO PROPANE

$O{=}\overset{\overset{O}{\|}}{N}\text{-}\overset{CH_3}{\underset{H}{C}}CH_3$

8. CHLOROBENZENE


9. TOLUENE


10. DIOXANE


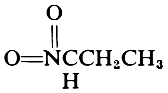
11. γ-BUTYROLACTONE


12. BENZENE


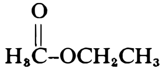
13. n-BUTYL ACETATE

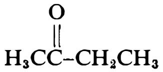
$H_3C\overset{\overset{O}{\|}}{C}\text{-}OCH_2CH_2CH_2CH_3$

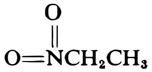
14. 2-BUTOXYETHANOL $H_3CCH_2CH_2CH_2OCH_2CH_2OH$

15. 1-NITROPROPANE

$O{=}\overset{\overset{O}{\|}}{N}\underset{H}{C}CH_2CH_3$

16. CELLOSOLVE $H_3CCH_2OCH_2CH_2OH$

17. ETHYL ACETATE

$H_3\overset{\overset{O}{\|}}{C}\text{-}OCH_2CH_3$

18. METHYL ETHYL KETONE

$H_3C\overset{\overset{O}{\|}}{C}\text{-}CH_2CH_3$

19. NITROETHANE

$O{=}\overset{\overset{O}{\|}}{N}CH_2CH_3$

20. METHYL CELLOSOLVE $H_3C\text{-}O\text{-}CH_2CH_2OH$

21. METHANOL $H_3COH$

obvious after considering these figures. For all three polymers it is the small, linear molecules which escape more rapidly than the larger, branched or cyclic molecules. Non-planar, cyclic molecules, such as cyclohexanone, escape very slowly. Smaller molecules start the second phase at a lower $M_0$ because of their greater plasticizing effectiveness and higher diffusion coefficients, and diffuse more rapidly out of the films.

The data on the retention of linear and cyclic solvents in Figures 5.8 and 5.9, respectively, are particularly useful in demonstrating the effect of molecular geometry. As the molecules become smaller and linear, less solvent is retained. The ether-alcohols are retained less than other solvents at long times. Their second phase evaporation curves are rather steep because of relatively high diffusion coefficients and the delay of the second phase due to slow evaporation in the first phase.

The retention curve for the presumably "non-hydrogen bonding" toluene in Vinylite VYHH is also interesting since toluene does not dissolve VYHH at room temperature. The solvent was absorbed into previously dried VYHH films at a higher temperature before exposure to air drying. Since toluene is retained slightly less than MIBK in poly(vinyl acetate), it was predicted prior to the experiment that toluene should be retained slightly less than MIBK in VYHH. This was indeed found to be the case. If further consideration is given to which of the solvents are retained most at the longest times reported, it will be seen that the order of retention is essentially the same regardless of the polymer. In other words, the reported curves can be used to estimate solvent retention in another polymer if one such retention curve for one of the solvents studied here is known for it. Figure 5.10 shows the approximate order of retention to be expected and is also the key to the curves in Figures 5.6, 5.7, 5.8, and 5.9. The first two solvents in Figure 5.10 are non-planar, which is the reason for their high degree of solvent retention.

### 5.7 *How to Measure Solvent Retention*

Solvent retention must be calculated after thorough drying of the samples. Flat-bottom Petri dishes are useful to determine proper drying conditions. The polymer should be dried in these at a temperature about 30° C above the $T_g$ of the polymer, preferably for 24 hrs. This polymer can then be dissolved in solvent added to the Petri dish. After solution, the solvent is allowed to evaporate and a uniform film will remain behind. The Petri dish can be weighed as desired, and dried under the same conditions as the pure polymer to determine approximate solvent content and whether or not this solvent can be removed by the heat treatment chosen. Weighings of films applied to tinned plates by spinning, followed by an oven drying, were used for all the data reported here. Isotopes can also be used to follow solvent retention (Hays 1964).

### 5.8 *Which Materials Retain Solvents?*

Some film forming materials retain solvent while others do not. When the polymer is of the type often referred to as a plastic, the chances of solvent retention are very high. If the $T_g$ of this material is below room temperature, however, solvent will not be retained in significant amounts at long times.

Some materials having high glass transition temperatures are known for their good "solvent release". Such materials are most often brittle resins of relatively low molecular weight which owe their high $T_g$'s to severe steric hindrance to motion. This evidently leads to higher diffusion coefficients due to sterically created "holes" in the material. At room temperature such a material appears to dry rapidly because it is far under its $T_g$ and the solvent which is retained has less apparent effect. Zinc resinate or maleic resins may be named as examples. The mathematics of diffusion emphasize that the percentage loss for the same diffusion coefficient and film thickness will be the same at a given time. Since $M_0$ is relatively high in these cases, the absolute loss is correspondingly larger giving a larger physical effect.

Some cellulosic materials dry very rapidly. Ethyl cellulose, for example, does not retain sufficient o-xylene for the second phase to be noted (Sletmoe 1966). This material does have a second phase drying period. Both o-xylene and methyl isobutyl ketone are retained in the same amounts, as would be predicted by considering the curves above. These amounts are not large after a day or two of drying. The solvent in these cases was essentially gone at a $t/(L')^2$ of $3 \times (10)^{10}$ sec/cm$^2$ or two or three days after application for a typical, 30 micron film thickness. Delay of the second phase for o-xylene masks its presence (see Section 7.6).

The retention of solvents in alkyds has also been studied. Here again solvent can be retained if the alkyd has a short oil length. The alkyds listed as R and D in Table 2.2 have short and long oil lengths, respectively. The long alkyd does not retain o-xylene; this alkyd has a sirupy consistency at room temperature, indicating diffusion coefficients will be high. The short alkyd does retain some o-xylene; this alkyd must be removed from a can by hammering, indicating polymer mobility is lower and lower diffusion coefficients. This latter alkyd retained about 1 weight per cent solvent for a 150 micron film after 1 day at room temperature.

### 5.9 *Conclusion*

The division of the process of solvent evaporation from polymer films into two distinct phases has enabled simple interpretation of numerous phenomena associated with film drying.

It is not always easy to say beforehand whether a given polymer will retain solvent or not, but when the problem occurs and is recognized, methods of solution have been outlined.

*Chapter 6*

# The Measurement of Concentration Dependent Diffusion Coefficients—The Exponential Case

## 6.1 *Introduction*

Concentration dependent diffusion coefficients with an exponential variation are of considerable interest since the diffusion coefficients of organic solvents in polymeric material vary in this manner at low concentration for every case known to the author. Generally these diffusion coefficients have been reported based on data interpreted with solutions to the diffusion equation with a constant diffusion coefficient. An error thus arises which must be corrected. Crank (1956A) has described methods for doing this by successive approximations which eventually lead to a better result, though these methods are rather tedious.

When the concentration dependence is exponential, such tedious correction procedures are not necessary, since the diffusion equation can be solved directly for this type variation. Comparison of these solutions with those where the diffusion coefficient is constant gives the error made in neglecting concentration dependence. Similar solutions for other types of concentration dependence would seem advisable where necessary.

## 6.2 *Mathematical Background*

Solutions to the diffusion equation, Fick's second law

6.1) $$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left[D_1(c)\frac{\partial c}{\partial x}\right]$$

have been evaluated for the case where the diffusion coefficients are given by

6.2) $$D_1(c) = D_0 e^{kc}$$

The calculations have been based on the thickness of a film attached to a substrate, L′. For absorption, the plane film was assumed to be at a uniform concentration initially, with the surface concentration rising immediately to $c_s$. There was no mass transfer through the substrate.

For desorption, the film was assumed to be at a uniform initial concentration, $c_o$, with the surface concentration immediately falling to zero. Here again there was no mass transfer through the substrate.

Some mathematical manipulation with these equations and boundary conditions allows considerable simplification for computer evaluation. In the manner given by Crank (1956B), Equation 6.1 can be expressed by

6.3) $$\frac{\partial C}{\partial T} = \frac{\partial}{\partial X}\left(D\frac{\partial C}{\partial X}\right)$$

where the symbols used are given below:

6.4) $T = D_o t/(L')^2$, reduced time

6.5) $X = \frac{x}{L'}$, reduced distance

6.6) $C = \frac{c - c_o}{c_s - c_o}$, reduced concentration

6.7) $K = (c_o - c_s)k$, for desorption

6.8) $K = (c_s - c_o)k$, for absorption

6.9) $D = \exp[K(1 - C)]$, for desorption

6.10) $D = \exp[KC]$, for absorption

6.11) $V = \exp[K]$, total variation

In this special case the auxiliary variable S, defined by

6.12) $$S = \frac{\int_0^C DdC}{\int_0^1 DdC}$$

allows further simplification of Equation 6.3 to

6.13) $$\frac{\partial D}{\partial T} = D\frac{\partial^2 D}{\partial X^2}$$

D and S are linearly related in the case of exponential dependence (B).

The boundary conditions corresponding to those listed above can be written as:

$T > 0, X = 0, D = 1$ for desorption
$D = e^K$ for absorption

$T > 0, X = 1, \frac{\partial D}{\partial X} = 0$ for both absorption and desorption

The initial conditions are

$$T = 0,\ 0 < X < 1,\ D = e^{K} \text{ for desorption}$$
$$D = 1 \quad \text{for absorption}$$

Equation 6.13 has been evaluated for various values of V for these boundary conditions by the Crank-Nicolson finite difference method (Crank 1956B) where the general equation is

$$6.14) \qquad D_m^{+} = D_m + \frac{(D_m^{+} + D_m)}{4.0}\frac{\Delta T}{(\Delta X)^2} \cdot$$
$$[D_{m-1} + D_{m-1}^{+} + D_{m+1} + D_{m+1}^{+} - 2(D_m + D_m^{+})]$$

A "+" indicates the next time increment while an "m" indicates a position in the film. For a film divided into m intervals, there are m of this type equations which must be solved simultaneously.

The boundary condition at the substrate was fulfilled by a fictitious interval to $X = 1.0 + \Delta X$ where the same concentrations prevailed as at $X = 1.0 - \Delta X$, and by continuing with Equation 6.14 at this point. Calculations were performed with 8, 16, and where necessary, 32 intervals with extrapolation of pertinent results to an infinite number of intervals to give the values reported in Table 6.1. The first entry in Table 6.1 is for a constant diffusion coefficient. The concentration gradients for these cases have been included in Appendix A–1 for absorption and in Appendix A–2 for desorption.

Table 6.1

| | Desorption | | | | Absorption | |
|---|---|---|---|---|---|---|
| V | $T_{\frac{1}{2}}$ | $T_{\frac{1}{4}}$ | $(F_d)_{\frac{1}{2}}$ | $(F_d)_{\frac{1}{4}}$ | $T_{\frac{1}{2}}$ | $(F_a)_{\frac{1}{2}}$ |
| $10^0$ | $1.94\times(10)^{-1}$ | $4.9\times(10)^{-2}$ | 1.00 | 1.00 | $1.94\times(10)^{-1}$ | 1.00 |
| 2 | $1.51\times(10)^{-1}$ | $3.80\times(10)^{-2}$ | 1.56 | 1.55 | $1.26\times(10)^{-1}$ | 1.3 |
| 5 | $1.05\times(10)^{-1}$ | $2.56\times(10)^{-2}$ | 2.70 | 2.61 | $6.60\times(10)^{-2}$ | 1.7 |
| $10^1$ | $7.80\times(10)^{-2}$ | $1.88\times(10)^{-2}$ | 4.0 | 3.84 | $3.90\times(10)^{-2}$ | 2.01 |
| $10^2$ | $2.60\times(10)^{-2}$ | $5.00\times(10)^{-3}$ | 13.4 | 10.2 | $6.40\times(10)^{-3}$ | 3.30 |
| $10^3$ | $8.40\times(10)^{-3}$ | $1.13\times(10)^{-3}$ | 43.3 | 23.1 | $9.40\times(10)^{-4}$ | 4.85 |
| $10^4$ | $2.69\times(10)^{-3}$ | $2.32\times(10)^{-4}$ | 138.7 | 47.4 | $1.19\times(10)^{-4}$ | 6.14 |
| $10^5$ | $8.60\times(10)^{-4}$ | $4.36\times(10)^{-5}$ | 443 | 89.0 | $1.48\times(10)^{-5}$ | 7.63 |
| $10^6$ | $2.66\times(10)^{-4}$ | $7.87\times(10)^{-6}$ | 1,370 | 160.5 | $1.74\times(10)^{-6}$ | 8.97 |
| $10^7$ | $8.36\times(10)^{-5}$ | $1.42\times(10)^{-6}$ | 4,300 | 290 | $2.05\times(10)^{-7}$ | 10.60 |
| $10^8$ | $2.65\times(10)^{-5}$ | $2.48\times(10)^{-7}$ | 13,670 | 506 | $2.35\times(10)^{-8}$ | 12.10 |

Note: These values supercede those reported previously (B).

### 6.3 *Correction Factors for Concentration Dependence*

The usual equation for calculating diffusion coefficients is based on the half-time of penetrant absorption or desorption found from the solution to the diffusion equation with a constant diffusion coefficient (Crank 1956A). For a free film of thickness L, this is:

$$6.15) \qquad T_{\frac{1}{2}} = \frac{D \cdot t_{\frac{1}{2}}}{L^2} = .049$$

or the average diffusion coefficient, $\bar{D}$, when the diffusion coefficient varies with concentration is found by:

$$6.16) \qquad \bar{D} = \frac{.049}{(t/L^2)_{\frac{1}{2}}} = \frac{.01225}{(t/L^2)_{\frac{1}{4}}}$$

Twice L′ would replace the total free film thickness L in this last equation if an attached film were being considered.

As is quite obvious from the data in Table 6.1, $T_{\frac{1}{2}}$ is not constant when the diffusion coefficient varies with concentration. Corrections to Equation 6.16 are therefore necessary according to the method used. Thus, for the diffusion coefficient at $c_0$ for desorption or $c_s$ for absorption, correction factors, $F_m$, must be applied according to Equation 6.17 for the half-time method.

$$6.17) \qquad D_1 = F_m \cdot \bar{D} = F_m \cdot \frac{.049}{(t/L^2)_{\frac{1}{2}}}$$

The correction factors $(F_a)_{\frac{1}{2}}$ for absorption measurements and $(F_d)_{\frac{1}{2}}$ for desorption measurements based on a ratio of half-times have been computed according to Equation 6.18.

$$6.18) \qquad (F_m)_{\frac{1}{2}} = \frac{T_{\frac{1}{2}}}{.194} \cdot (V)$$

The constant in this equation is 0.194 rather than 0.049 because the present calculations are based on L′ rather than L.

Similar corrections based on quarter-times for desorption have been calculated because of the extremely long experimental times involved for low diffusion coefficients. These factors, $(F_d)_{\frac{1}{4}}$, are listed in Table 6.1 for use in Equation 6.19.

$$6.19) \qquad D_1 = (F_d)_{\frac{1}{4}} \cdot \frac{0.01225}{(t/L^2)_{\frac{1}{4}}}$$

### 6.4 *Experimental*

Diffusion coefficient measurements at 25° have been performed for methanol, ethylene glycol monomethyl ether (EGMME), chlorobenzene, and cyclohexanone

Table 6.2
Diffusion Coefficients for Methanol in Poly(vinyl Acetate) at 25° C.

| $c_o$, vol. fract. | $c_s$, vol. fract. | $\bar{D}$, cm²/sec. | V, Decades | $F_m$ | $D_1$, cm²/sec. |
|---|---|---|---|---|---|
| | | Absorption Half-time Technique | | | |
| .025 | .0497 | $2.2 \times (10)^{-9}$ | .44 | 1.44 | $3.17 \times (10)^{-9}$ |
| .0497 | .0744 | $8.16 \times (10)^{-9}$ | .45 | 1.45 | $1.18 \times (10)^{-8}$ |
| 0 | .110 | $1.19 \times (10)^{-8}$ | 1.93 | 3.26 | $3.88 \times (10)^{-8}$ |
| | | Desorption Half-time Technique | | | |
| .0278 | 0 | $7.84 \times (10)^{-10}$ | .37 | 1.73 | $1.36 \times (10)^{-9}$ |
| .0453 | 0 | $9.72 \times (10)^{-10}$ | .79 | 3.10 | $3.01 \times (10)^{-9}$ |
| .0553 | 0 | $1.12 \times (10)^{-9}$ | .97 | 3.88 | $4.35 \times (10)^{-9}$ |
| .0744 | 0 | $1.75 \times (10)^{-9}$ | 1.31 | 5.85 | $1.02 \times (10)^{-8}$ |
| .1131 | 0 | $4.02 \times (10)^{-9}$ | 2.0 | 13.4 | $5.39 \times (10)^{-8}$ |

Table 6.3
Diffusion Coefficients for Ethylene Glycol Monomethyl Ether
in Poly(vinyl Acetate) at 25° C

| $c_o$, vol. fract. | $c_s$, vol. fract. | $\bar{D}$, cm²/sec. | V, Decades | $F_m$ | $D_1$, cm²/sec. |
|---|---|---|---|---|---|
| | | Absorption Half-time Technique | | | |
| .0516 | .087 | $1.472 \times (10)^{-8}$ | .89 | 1.89 | $2.79 \times (10)^{-8}$ |
| .0858 | .119 | $9.25 \times (10)^{-10}$ | .81 | 1.81 | $1.67 \times (10)^{-9}$ |
| .114 | .141 | $3.90 \times (10)^{-9}$ | .66 | 1.66 | $6.48 \times (10)^{-9}$ |
| .141 | .178 | $7.24 \times (10)^{-9}$ | $.\bar{3}$ | $1.\bar{3}$ | $9.40 \times (10)^{-9}$ |
| | | Desorption Half-time Technique | | | |
| .0669 | 0 | $9.60 \times (10)^{-12}$ | 1.67 | 8.9 | $8.54 \times (10)^{-11}$ |
| | | Desorption Quarter-time Technique | | | |
| .0329 | 0 | $4.50 \times (10)^{-12}$ | .80 | 2.9 | $1.30 \times (10)^{-11}$ |
| .0669 | 0 | $9.60 \times (10)^{-12}$ | 1.67 | 7.6 | $7.30 \times (10)^{-11}$ |
| .0893 | 0 | $2.01 \times (10)^{-11}$ | 2.23 | 12.6 | $2.53 \times (10)^{-10}$ |
| .119 | 0 | $7.53 \times (10)^{-11}$ | 2.95 | 22.5 | $1.69 \times (10)^{-9}$ |

in poly(vinyl acetate), Mowilith 50, donated by Farbwerke Hoechst AG, Frankfort (M). Tables 6.2, 6.3, 6.4 and 6.5 include data from these measurements.

An apparatus similar to one described previously (Prager and Long 1951) was placed in a constant temperature room for measuring rates of absorption at various penetrant vapor pressures, and rates of desorption under vacuum. A mechanical pressure gauge which was particularly sensitive in the range of 1 to 10

Table 6.4

Diffusion Coefficients for Chlorobenzene in Poly(vinyl Acetate) at 25° C

| $c_0$, vol. fract. | $c_s$, vol. fract. | $\bar{D}$, cm²/sec. | V, Decades | $F_m$ | $D_1$, cm²/sec. |
|---|---|---|---|---|---|
| | | Desorption Quarter-time Technique | | | |
| .120 | 0 | $1.28 \times (10)^{-12}$ | 3.73 | 40 | $5.12 \times (10)^{-11}$ |
| .130 | 0 | $2.40 \times (10)^{-12}$ | 4.05 | 50 | $1.20 \times (10)^{-10}$ |
| .147 | 0 | $5.32 \times (10)^{-11}$ | 4.58 | 69.5 | $3.70 \times (10)^{-10}$ |
| .151 | 0 | $8.38 \times (10)^{-12}$ | 4.70 | 74 | $6.20 \times (10)^{-10}$ |
| .173 | 0 | $2.94 \times (10)^{-11}$ | 5.38 | 112 | $3.29 \times (10)^{-9}$ |
| .186 | 0 | $5.10 \times (10)^{-11}$ | 5.80 | 144 | $7.35 \times (10)^{-9}$ |
| | | Absorption Half-time Technique | | | |
| .112 | .138 | $1.04 \times (10)^{-10}$ | .8 | 1.80 | $1.87 \times (10)^{-10}$ |
| .138 | .161 | $6.17 \times (10)^{-10}$ | .70 | 1.70 | $1.05 \times (10)^{-9}$ |
| .152 | .188 | $1.77 \times (10)^{-9}$ | 1.1 | 2.12 | $3.76 \times (10)^{-9}$ |
| .202 | .230 | $1.19 \times (10)^{-8}$ | – | – | – |
| .230 | .282 | $1.83 \times (10)^{-8}$ | – | – | – |

Table 6.5

Diffusion Coefficients for Cyclohexanone in Poly(vinyl Acetate) at 25° C.

| $c_0$, vol. fract. | $c_s$, vol. fract. | $\bar{D}$, cm²/sec. | V, Decades | $F_m$ | $D_1$, cm²/sec. |
|---|---|---|---|---|---|
| | | Desorption Quarter-time Technique | | | |
| .150 | 0 | $4.05 \times (10)^{-13}$ | 3.97 | 48 | $1.94 \times (10)^{-11}$ |
| .181 | 0 | $2.12 \times (10)^{-12}$ | 4.80 | 79 | $1.68 \times (10)^{-10}$ |
| .190 | 0 | $2.76 \times (10)^{-12}$ | 5.05 | 92 | $2.54 \times (10)^{-10}$ |
| .229 | 0 | $1.51 \times (10)^{-11}$ | 6.07 | 170 | $2.57 \times (10)^{-9}$ |
| | | Absorption Half-time Technique | | | |
| .177 | .210 | $4.76 \times (10)^{-10}$ | .87 | 1.87 | $8.92 \times (10)^{-10}$ |
| .260 | .270 | $1.22 \times (10)^{-8}$ | $\bar{1}$ | $1.\bar{1}$ | $1.34 \times (10)^{-8}$ |
| .266 | .288 | $1.52 \times (10)^{-8}$ | $.\bar{1}$ | $1.\bar{1}$ | $7.67 \times (10)^{-8}$ |

mm. of mercury was necessary because of the low vapor pressures of several of the penetrants. Aluminum backed films were prepared in the range of 15 to 120 microns in thickness by dipping a 5 micron thick aluminum foil supported in a frame in a solution of the polymer and drawing it up slowly (B). Up to four of these films were supported by thin wire on a calibrated quartz spiral having a maximum allowable load of about 0.5 grams. Diffusion coefficients were deduced from the extension of the spiral as a function of time. A sketch of this apparatus is included in Figure 5.5. The portion connected with torsion pendulum measurements was closed off for these measurements.

The unit of length used in the calculations was the dried film thickness found from the sample weight after drying 6 hours at 95° C. No problems with abnormal diffusion curves were encountered as long as the concentrations were within the range which could be represented by the exponential model. An exception to this was an induction period which was apparently necessary when solvent was absorbed by the freshly dried films. A film from which methanol had been evaporated was used in one case for absorption from zero concentration with a normal absorption curve. At concentrations somewhat higher than those for which data are reported, surface resistance to mass transfer becomes significant and the data can not be interpreted properly without accounting for this fact. (See Chapter 7).

### 6.5 *Use of the Correction Factors*

After obtaining $\bar{D}$ data at a number of concentrations from Equation 6.16, an approximate $D_0$ can be found by extrapolation to zero concentration. This enables approximate variations to be estimated and the corresponding correction factors for use in Equation 6.17 or 6.19 can be found from the data in Table 6.1. Thus, an approximate $D_1$ curve can be established with no difficulty. Variations are then found from this curve and appropriate correction factors are again applied to the $\bar{D}$ data. This process can be repeated again, if necessary, though in most cases no more than two iterations should be necessary. This has been done graphically in the present study. The data reported illustrate use of the correction factors for each technique.

Because of lower correction factors, absorption measurements are to be preferred where possible. In the case of cyclohexanone, the vapor pressure is so low that a constant surface concentration is difficult to maintain for absorption experiments. In this case desorption gives more reliable data. After a uniform film has been obtained by absorption to a constant composition, for example, one need only turn on the vacuum pump and observe the rate of loss of solvent. The length of the experiments becomes prohibitively long at low diffusion coefficients, however, and the correction factors are high leading to some uncertainty in the final result, particularly where long extrapolations are involved.

These corrections are applicable to data reported elsewhere in the literature where such have not been made by other techniques. Crank (1956A) has corrected his data on the diffusion of chloroform in polystyrene at 25° by the integral technique. If one applies the corrections suggested here to the best line though his $\bar{D}$ values, one arrives at the best line though his corrected data. The two methods are equivalent in this case. $D_0$ from Crank's data was found as $3.7 \times (10)^{-13}$ cm$^2$/sec and k was 41.7 where concentration is expressed as % regain at equilibrium.

The data reported by Kishimoto and Matsumoto (1964) also assume a new significance when these corrections are applied. It can be seen that steady state, absorption, and desorption data give the same result.

The averaging of absorption and desorption data is sometimes done to find an average diffusion coefficient. This does not give a better result, since the values found by both of these methods are too low when the diffusion coefficient increases with increasing concentration. Desorption data will give lower results than absorption data. This is because in both cases there will always be diffusion though a region of lower concentration than that ascribed to the experiment, and in desorption experiments a greater portion of the experiment occurs at proportionally lower concentrations than in absorption experiments. For this reason desorption half-times are the least reliable of the methods described here since a greater portion of the experiment takes place at concentrations far removed from the single concentration ascribed to the experiment.

### 6.6 *Discussion of Results*

As can be seen from the results in Figure 6.1, the corrected diffusion coefficients in poly(vinyl acetate) of the four solvents studied can be represented by the exponential variation at low concentration. Values of $D_0$ and k for these cases are given in Table 6.6.

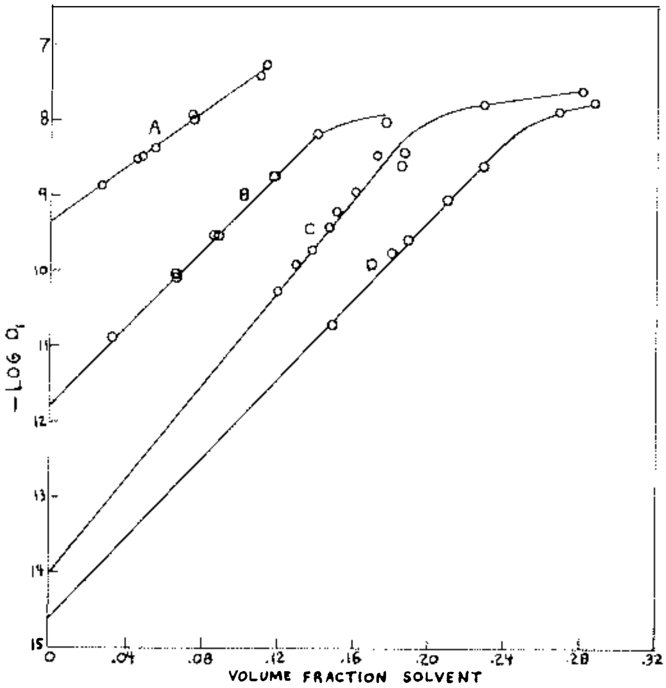


Figure 6.1. Diffusion coefficients in poly(vinyl acetate) at 25° for: A methanol, B ethylene glycol monomethyl ether, C chlorobenzene, D cyclohexanone

Table 6.6

Diffusion Coefficient Constants for Organic Liquids in Poly(vinyl Acetate) at 25° C.

| | $D_o$, cm³/sec. | k, (vol. fract.)⁻¹ |
|---|---|---|
| Methanol | $4.46 \times (10)^{-10}$ | 41 |
| Ethylene glycol monomethyl ether | $1.78 \times (10)^{-12}$ | 58 |
| Chlorobenzene | $1.0 \times (10)^{-14}$ | 71 |
| Cyclohexanone | $2.5 \times (10)^{-15}$ | 61 |

The diffusion coefficients for cyclohexanone were expected to be lower than those for chlorobenzene because its non-planar ring requires a larger piece of unoccupied space to be able to move than the planar chlorobenzene. The linear structure of the EGMME molecule enables it to diffuse faster than the ring compounds but not so fast as the still smaller methanol molecule.

There is no evident correlation of diffusion coefficients with hydrogen or polar bonding tendencies of the solvents. Molecular size and shape are evidently far more important in determining the diffusion of solvents in polymers than such solvent-polymer bonds. This has been pointed out in Chapter 5 based on data on the escape of solvents from polymer films laid down from solution. Similarly, energies of activation for diffusion in poly(vinyl acetate) support the hole formation theory (Kokes and Long 1953).

If one prepares poly(vinyl acetate) films from solutions of each of these four solvents, a 50 micron film after one month will contain essentially no methanol, 0.024 volume fraction EGMME, 0.059 volume fraction chlorobenzene, or 0.095 volume fraction cyclohexanone. The same film laid down from cyclohexanone will still contain almost 0.04 volume fraction solvent after 10 years. Polymers with higher glass transitions temperatures can be expected to retain still more solvent. Low diffusion coefficients lead to greater solvent retention.

The rapid variation in diffusion coefficient with increasing solvent content is due to the very strong plasticizing action of the solvent. Greater polymer chain segment mobility is promoted with increasing solvent concentration and consequently solvent diffusion coefficients increase.

## 6.7 *Steady State*

To complete this study of exponential diffusion coefficients, the steady state permeation through a film will be discussed briefly. The analytical solution to Equation 6.13 can be found directly yielding the mass flux as

20) $$Q = \frac{D_0}{kL} \left( e^{kc_1} - e^{kc_2} \right)$$

where $c_1$ and $c_2$ are the concentrations at the two surfaces. If $c_2$ is taken as zero, $D_0$ can be found from a plot of Log Q versus $c_1$ for varying $c_1$. The slope of this plot will be k at higher concentrations, and the intercept is $\mathrm{Log}(D_0/kL)$. Long (1965) has discussed practical implications of permeation with this type diffusion coefficient.

## 6.8 *Conclusion*

The use of simple correction factors to account for concentration dependence in the measurement of diffusion coefficients has been demonstrated. These correction factors are based on solutions for the diffusion equation for an exponential dependence though other variations could also be treated in a similar manner. Whenever concentration dependence is encountered, some form of correction is necessary to deduce true diffusion coefficients. The diffusion coefficients of organic solvents in high polymers vary exponentially with concentration at low solvent concentrations. Their absolute values are strongly dependent on the molecular structure of the penetrant. Where diffusion coefficients are low, solvent can be retained over a period of years in films formed from solution.

### *Nomenclature for this Chapter*

| | |
|---|---|
| c | Concentration |
| t | Time |
| x | Distance |
| $D_1$ | True diffusion coefficient |
| $D_0$ | Diffusion coefficient at lowest concentration in an experiment (assumed zero) |
| k | See Equation 6.2 |
| $c_s$ | Surface concentration |
| $c_0$ | Initial concentration |
| L′ | Film thickness of a film attached to a substrate |
| L | Film thickness of free film |
| T | Defined by Equation 6.4 |
| X | Defined by Equation 6.5 |
| C | Defined by Equation 6.6 |
| K | Defined by Equation 6.7 or 6.8 |
| D | Defined by Equation 6.9 or 6.10 |
| V | Defined by Equation 6.11 |
| S | Defined by Equation 6.12 |
| $\bar{D}$ | Averaged diffusion coefficient |
| $F_m$ | Correction factor to be applied to $\bar{D}$ according to method used |
| Q | Mass flux at steady state |
| $c_1$ | Concentration at surface of film with highest concentration |
| $c_2$ | Concentration at surface of film with lowest concentration |

*Special Subscripts*

| | |
|---|---|
| $\frac{1}{2}$ | Based on half-times |
| $\frac{1}{4}$ | Based on quarter-times |
| a | Absorption |
| d | Desorption |

## Chapter 7

# A Mathematical Description of Solvent Evaporation

### 7.1 *Introduction*

The purpose of this chapter is to examine the mathematics of solvent evaporation in an effort to duplicate the drying curve exemplified in Figure 5.2 by a mathematical analysis. In the previous section the diffusion coefficients of solvents in poly(vinyl acetate) were shown to be exponentially dependent on concentration at low concentrations. Diffusion coefficients have also been measured for chlorobenzene in this same polymer at higher solvent concentrations. This was done since the drying process involves internal diffusion in the concentration range of zero to the concentration of the solution from which the film is made. The general variation of the diffusion coefficient for solvents can be expected to be essentially the same in other polymers, assuming no special consideration, such as gel formation or partial crystallinity, are involved. This means the results of these calculations can be used for other systems and polymers than those studied here if the necessary constants are known or can be estimated.

### 7.2 *Diffusion Coefficients for Chlorobenzene in Poly(vinyl Acetate)*

The diffusion coefficients of chlorobenzene labelled with the isotope $Cl^{36}$ have been measured at 0.59 and 0.76 volume fraction chlorobenzene in poly(vinyl acetate). The method used in these measurements has been described previously (Walker 1950), though some details of technique have been changed due to the materials involved. This technique actually measures self-diffusion at a given polymer concentration.

A sketch of the apparatus used is given in Figure 7.1. Since the isotope is a beta emitter, thin-walled glass tubes having an equivalent wall thickness of about 30 mg/cm$^2$ were used. These tubes were 6–7 mm in diameter. The half-life of the isotope is $4.4 \times (10)^5$ years. The ASTM size 80 copper net was necessary to prevent mechanical mixing on addition of the active solution. Testing with dyed solutions showed no mechanical mixing occurred when the active solution was carefully added directly on the center of the net after the net had been carefully pushed into the interface. The net was held in place by three small legs which gently pushed against the walls of the glass tube.

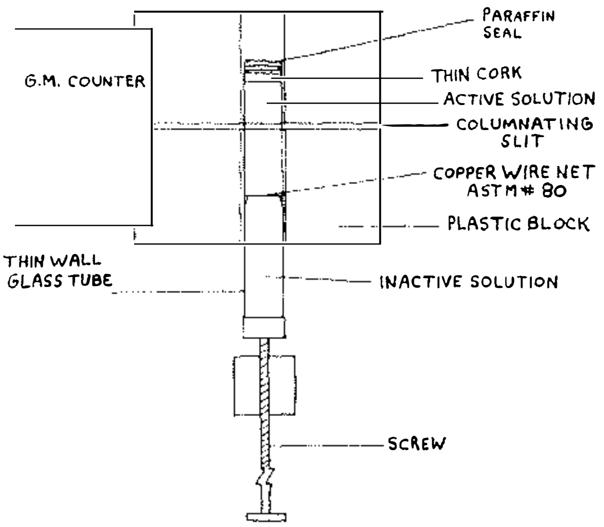


Figure 7.1. Cross sectional sketch of apparatus for isotopic diffusion coefficient measurements

The activity at various points in the tube could be measured by a G-M counter at various times after starting the experiment. The width of the columnating slit was 1 mm, and its length was 15 mm. These activities could be used to calculate diffusion coefficients from data taken up to the point where activities at the ends of the tube were still unaltered. Assuming the volumes of active and non-active solutions were equal:

7.1) $$A_x = \frac{A_0}{2} [1 - \mathrm{Erf}\ y]$$

where

7.2) $$y^2 = \frac{x^2}{4D_c t}$$

here

$A_x$ = activity at distance x from interface
$A_0$ = initial activity in active portion of glass tube
$x$ = distance from interface
$t$ = time
$D_c$ = diffusion coefficient

For each measurement, erf y could be calculated from activity data. Erf y as a function of y is available in standard tables (Crank 1956 C), enabling calculation of $D_c$ from Equation 7.2.

A summary of the results of these measurements is given in Table 7.1.

Table 7.1

Diffusion Coefficients of Chloro-36-Benzene in Poly(vinyl Acetate) at 23° C.

| Experiment | Volume fraction chlorobenzene | $D_c$ $(10)^6$ cm²/sec | No. of observations | Standard deviation × $(10)^6$ | Standard deviation of average × $(10)^6$ |
|---|---|---|---|---|---|
| 1 | 0.76 | 8.98 | 26 | 2.62 | 0.51 |
| 1A | 0.76 | 8.96 | 9 | 2.77 | 0.92 |
| 2 | 0.59 | 3.02 | 4 | 0.18 | 0.09 |

In addition to these diffusion coefficients, the self-diffusion coefficient for pure chlorobenzene has been interpolated from data abstracted by Bird et al. (Bird, Stewart, and Lightfoot 1960) from a review article by Johnson and Babb (1956). This value is $1.65 \times (10)^{-5}$ cm²/sec. at 25° C.

Combining these diffusion coefficients with those in the preceding section for the same system enables estimation of the diffusion coefficients for this system over the entire concentration range as shown in Figure 7.2. Additional diffusion

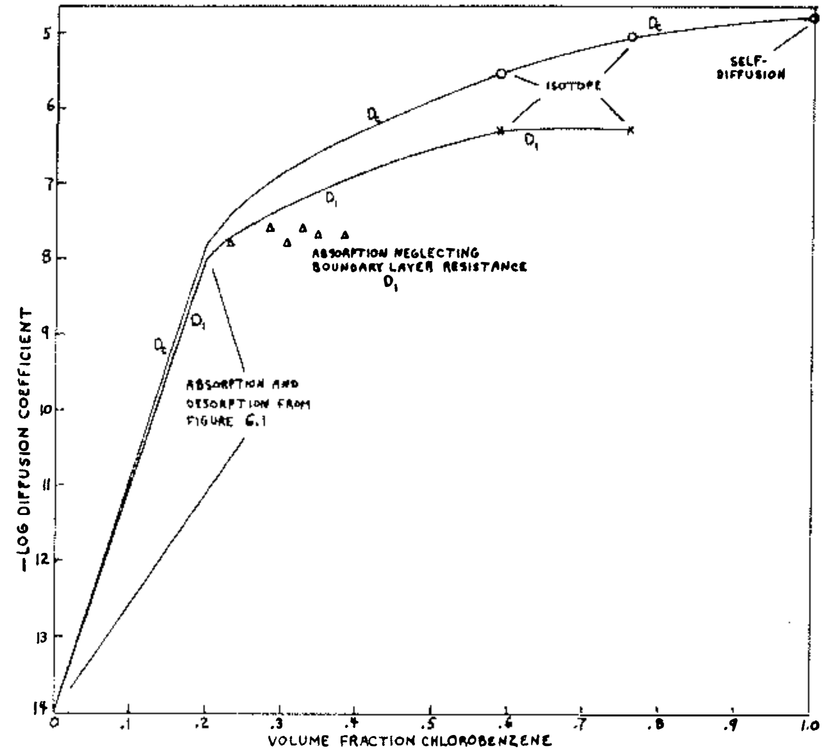


Figure 7.2. Diffusion coefficients for chlorobenzene in poly(vinyl acetate)

coefficient data from absorption measurements are included in this figure to show that the effect of surface resistance must be considered in these diffusion coefficient measurements at higher solvent concentrations. This also supports the conclusion that boundary layer resistance affects solvent evaporation down to concentrations near those at the break in the drying curve, $M_0$. $M_0$ is very close to $C_A$, the concentration at which the exponential variation in the diffusion coefficients ceases to be valid.

### 7.3 *The Mathematical Model for Solvent Evaporation*

The variation of the diffusion coefficient of a solvent in a polymer, in this case chlorobenzene in poly(vinyl acetate), with solvent concentration is known. This knowledge combined with the diffusion equation and a surface boundary resistance to solvent evaporation should enable calculation of the entire drying process for evaporation of a typical solvent from a typical film forming polymer.

Certain mathematical conveniences have been employed in the solution of this problem. To avoid the problem of changing total film thickness when solvent evaporates, the diffusion coefficients and unit of length have been based on the volume of dry polymer in the film. The diffusion coefficients based on the total volume of the film are related to those based on the amount of polymer present by Equation 7.3.

$$D_1(c) = D_c(c)(1 - v_f)^2 \tag{7.3}$$

where

$D_1(c)$ = diffusion coefficient based on dry polymer volume
$D_c(c)$ = diffusion coefficient based on total volume
$v_f$ = volume fraction of solvent

Both of these diffusion coefficients are plotted in Figure 7.2. The entire mathematical development in the preceding chapter can be carried over for present purposes since the variation given in Figure 7.2 has been approximated by two exponentially varying portions as described in Figure 7.3. The variables given in this figure could be altered to explore various variations of $D_1(c)$.

The only addition to the mathematical analysis in the preceding section is that the boundary layer resistance must be included, replacing the assumption of no resistance to solvent transport at $X = 0$. The mass flux was assumed to be directly proportional to the surface concentration to a first approximation. This is expressed mathematically by Equation 7.4 where the flux, F, just within the surface has been equated to that just outside the surface.

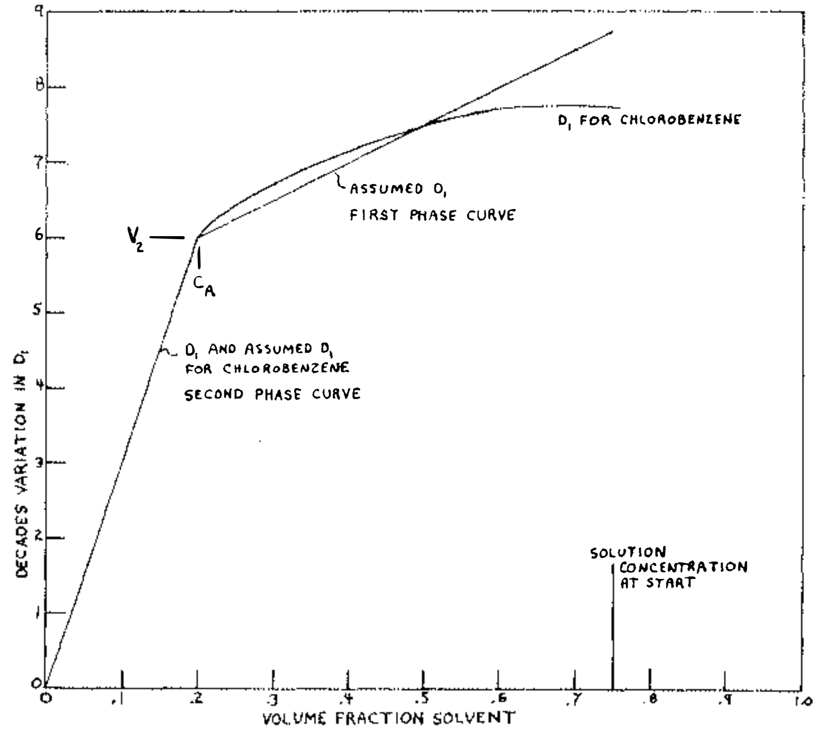


Figure 7.3. Assumed diffusion coefficient variations for computer evaluation of solvent evaporation from polymer films

7.4) $$F = -D_{1s}\frac{dc_s}{dx} = hc_s$$

$D_{1s}$ = diffusion coefficient at surface concentration
$c_s$ = surface concentration
$x$ = distance-positive into the film
$h$ = surface mass transfer coefficient

After some manipulation with the variables in the previous chapter, this condition can be expressed in dimensionless terms as

7.5) $$\frac{dD_s}{dX} = B \ln(D_s)$$

where $D_s$ is the reduced diffusion coefficient found by inserting $c_s$ in Equation 6.6 and the resulting $C_s$ in Equation 6.9. B is given by Equation 7.6 as the resistance to mass transport by internal diffusion, $R_d$, divided by the resistance to mass transport by surface resistance, $R_s$.

7.6) $$B = \frac{R_d}{R_s} = \frac{L'/D_0}{1/h} = \frac{hL'}{D_0}$$

In the following, $D_0$ is generally thought of as being constant, so that for a given film thickness, a high B is indicative of low surface resistance, and conversely, a low B means high surface resistance which may be thought of as approaching the case of plasticizer evaporation.

The value of $D_s^+$ can be calculated from Equation 7.5 in finite difference form. This finite difference equation is

$$7.7) \qquad D_s^+ = D_s + \tfrac{1}{2}\frac{\Delta T}{(\Delta X)^2}(D_s^+ + D_s)\cdot$$
$$[D_{s+1} + D_{s+1}^+ - D_s - D_s^+ - B(\ln D_s + \ln D_s^+)\Delta X]$$

in agreement with the mathematical background described in the previous sections.

To sum up then, the mathematical model involves solution of the diffusion equation with an exponential variation in the diffusion coefficient and a surface boundary resistance. The diffusion equation, Equation 6.1, can be generalized to give Equation 6.13, and the boundary resistance can be expressed by Equation 7.5. Equations 6.13 and 7.5 can then be treated in terms of finite differences to give Equations 6.14 and 7.7. These were the equations directly used in the computer evaluations. The diffusion coefficients were assumed as shown in Figure 7.3.

## 7.4 *The Evaluation of Constants for the Mathematical Model*

The mathematical model described in the previous section has been developed without regard to absolute values for the various constants involved. They have all been treated as dimensionless quantities since each of the variables is expressed as a ratio. The solutions found are general. The effect of film thickness, for example, is included in the time variable, $D_0t/(L')^2$, and distance varies from 0 to 1.0 instead of from 0 to L′. The relative diffusion coefficient used in the evaluations varies from 1 to some almost astronomical value of $10^6$ or $10^7$ for the second phase variation, and still more if the first phase is also included. These dimensionless numbers have relation to reality; one need only evaluate the absolute constants and put them into the completely general solutions to get the desired answer.

The diffusion of chlorobenzene in poly(vinyl acetate) will be taken as an example. $D_0$ is $10^{-14}$ cm²/sec. From Figure 7.3, $V_2$ is $10^6$ and $C_A$ is 0.2 volume fraction solvent. Extrapolation of the assumed first phase diffusion coefficient curve in this figure to an intercept gives a value of $10^{10}$ as a total variation, $V_t$. This value is used to calculate the slope of the first phase diffusion coefficient curve only and has no physical significance. The initial concentration is taken as 0.75 volume fraction solvent.

B can be estimated since it is known that the boundary layer resistance and diffusional resistance are approximately equal near the break in the drying curve.

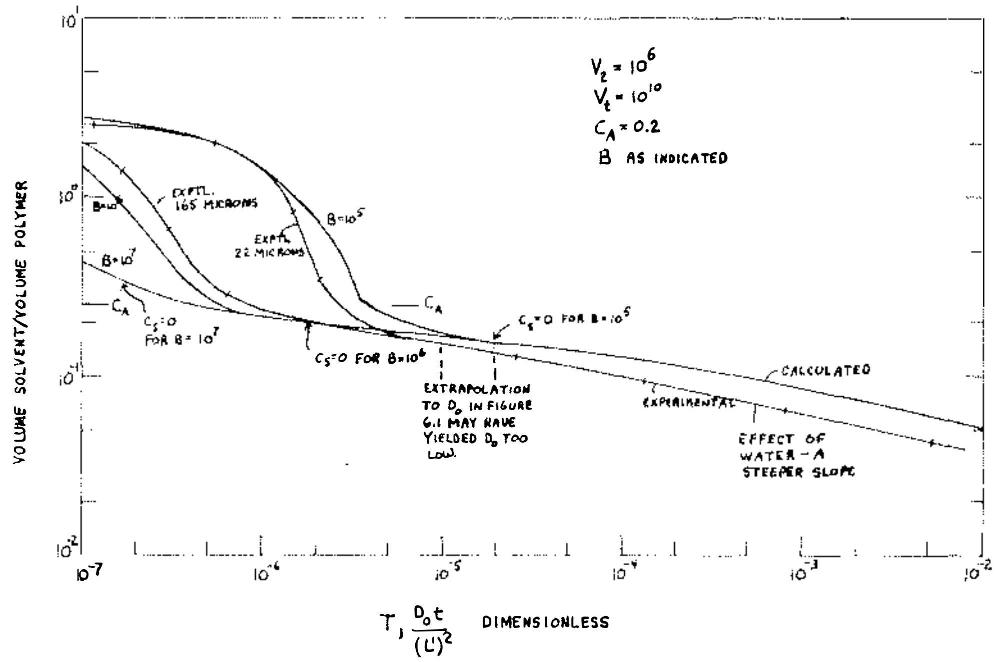


Figure 7.4. Calculated and experimental drying curves for the evaporation of chlorobenzene from poly(vinyl acetate)

In other words since D is about $10^6$ at $C_A$ and since $C_A$ is about equal to $M_0$, the concentration at the break in the drying curve, B can be assumed close to $10^6$. Results of calculations using these constants with assumed B values of $10^5$, $10^6$, and $10^7$ are given in Figures 7.4 and 7.5.

### 7.5 *Calculated Drying Curves and Concentration Gradients*

The constants evaluated in the previous section have been used in solutions to the mathematical model for solvent evaporation. These results are given in Figure 7.4 where various values of B have been assumed. Included in the same figure are evaporation data for chlorobenzene from poly(vinyl acetate). The calculated curves have a distance between them in the first phase corresponding to a factor of the ratio of the B values, which again says the ratio of their thicknesses, assuming $D_0$ and h are the same in each case. This was found in the evaporation curves shown in Figures 5.1 and 5.2 also.

A B of $10^7$ is too high for ordinary air drying, and would correspond to reducing boundary layer resistance by blowing air past the surface. Regardless of the B value, the second phase curves coincide. Subcooling, turbulence in the drying film, and all the other effects accompanying these factors have been neglected in this simplified treatment. In reality, B varies during drying because of these factors, but a rigorous treatment would be extremely difficult.

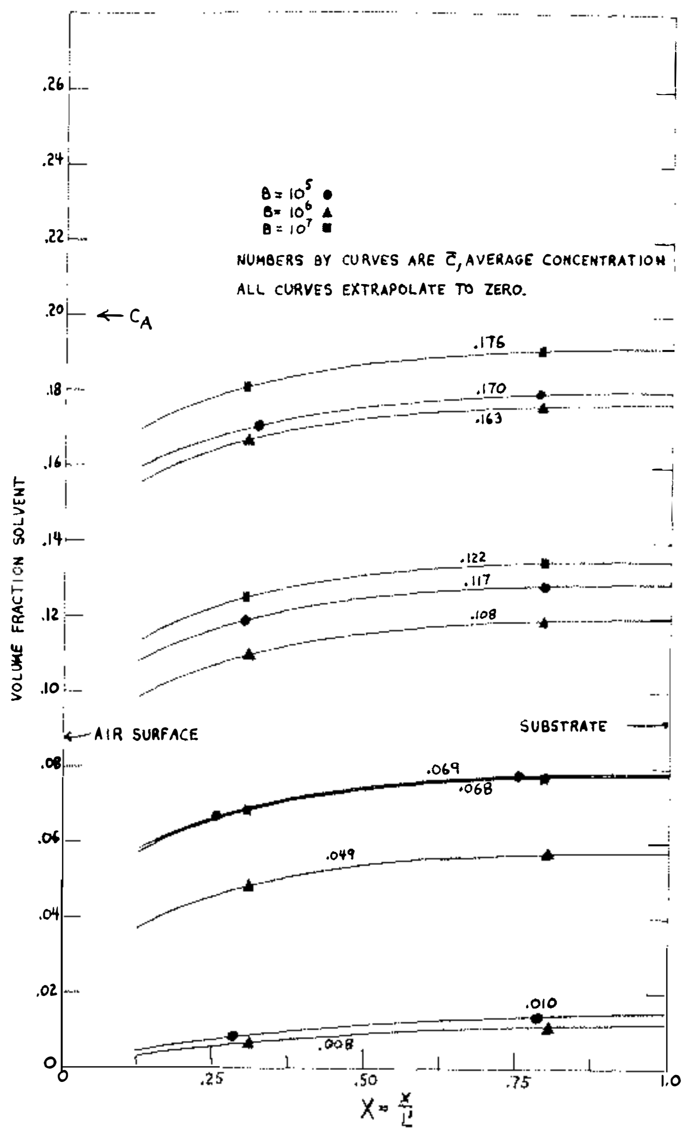


Figure 7.5. Calculated concentration gradients during evaporation of chlorobenzene from poly(vinyl acetate)

Calculations showed that varying the slope of the first phase diffusion coefficient curve in Figure 5.3 had no effect on the second phase drying curve. The discrepancy between the assumed diffusion coefficients and the true ones does not affect the result in the first stages of evaporation. The film is for all practical purposes uniform in concentration in the first phase, since the diffusion coefficients are high enough to allow free movement of solvent within the film, the major resistance

Table 7.2

Calculated Concentration Gradients for the Evaporation of Chlorobenzene from Poly (vinyl Acetate). Concentrations in Volume Fractions

| B | LOG T | $\bar{C}$ | X | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | 0 | 0.125 | 0.250 | 0.375 | 0.500 | 0.625 | 0.750 | 0.875 | 1.000 |
| $10^5$ | −5.231 | .1699 | .0985 | .1591 | .1679 | .1726 | .1756 | .1775 | .1787 | .1794 | .1796 |
| | −4.875 | .1449 | .0154 | .1364 | .1454 | .1502 | .1532 | .1552 | .1565 | .1572 | .1574 |
| | −4.141 | .1169 | .0000 | .1078 | .1168 | .1268 | .1246 | .1266 | .1278 | .1285 | .1288 |
| | −3.410 | .0929 | .0000 | .0828 | .0918 | .0966 | .0996 | .1015 | .1028 | .1035 | .1037 |
| | −2.663 | .0690 | .0000 | .0579 | .0668 | .0716 | .0746 | .0766 | .0778 | .0785 | .0787 |
| | −1.915 | .0454 | .0000 | .0339 | .0423 | .0469 | .0498 | .0518 | .0530 | .0537 | .0539 |
| | −1.362 | .0286 | .0000 | .0180 | .0251 | .0293 | .0320 | .0338 | .0349 | .0358 | .0358 |
| | −0.635 | .0098 | .0000 | .0042 | .0072 | .0095 | .0111 | .0123 | .0131 | 0136 | .0137 |
| $10^6$ | −6.099 | .1842 | .0269 | .1769 | .1859 | .1907 | .1937 | .1957 | .1970 | .1977 | .1979 |
| | −5.559 | .1626 | .0000 | .1554 | .1645 | .1693 | .1723 | .1742 | .1755 | .1762 | .1764 |
| | −4.638 | .1321 | .0000 | .1237 | .1327 | .1375 | .1405 | .1425 | .1438 | .1445 | .1447 |
| | −3.891 | .1081 | .0000 | .0987 | .1077 | .1125 | .1155 | .1175 | .1187 | .1194 | .1196 |
| | −3.328 | .0902 | .0000 | .0799 | .0889 | .0937 | .0967 | .0987 | .0999 | .1006 | .1009 |
| | −2.765 | .0722 | .0000 | .0613 | .0702 | .0750 | .0780 | .0799 | .0812 | .0819 | .0821 |
| | −2.016 | .0485 | .0000 | .0370 | .0456 | .0502 | .0532 | .0551 | .0563 | .0570 | .0572 |
| | −1.461 | .0315 | .0000 | .0206 | .0281 | .0323 | .0351 | .0369 | .0381 | .0388 | .0390 |
| | −0.913 | .0162 | .0000 | .0082 | .0130 | .0162 | .0184 | .0199 | .0209 | .0215 | .0217 |
| | −0.553 | .0081 | .0000 | .0033 | .0058 | .0078 | .0092 | .0103 | .0110 | .0114 | .0116 |
| $10^7$ | −7.671 | .4585 | .1614 | .3879 | .4412 | .4694 | .4870 | .4986 | .5059 | .5101 | .5114 |
| | −7.119 | .3189 | .0221 | .2466 | .3009 | .3296 | .3477 | .3595 | .3671 | .3713 | .3727 |
| | −6.575 | .2180 | .0000 | .1885 | .1976 | .2143 | .2323 | .2441 | .2517 | .2559 | .2573 |
| | −6.021 | .1763 | .0000 | .1698 | .1788 | .1836 | .1866 | .1886 | .1898 | .1905 | .1908 |
| | −5.085 | .1463 | .0000 | .1385 | .1475 | .1523 | .1553 | .1573 | .1585 | .1592 | .1595 |
| | −4.335 | .1223 | .0000 | .1134 | .1225 | .1273 | .1303 | .1322 | .1335 | .1342 | .1344 |
| | −3.584 | .0983 | .0000 | .0884 | .0974 | .1022 | .1052 | .1072 | .1085 | .1092 | .1094 |
| | −2.645 | .0684 | .0000 | .0573 | .0662 | .0710 | .0740 | .0760 | .0772 | .0779 | .0781 |
| | −1.712 | .0391 | .0000 | .0277 | .0358 | .0403 | .0432 | .0451 | .0463 | .0470 | .0472 |
| | −1.164 | .0229 | .0000 | .0132 | .0195 | .0233 | .0258 | .0275 | .0286 | .0293 | .0295 |
| | −0.620 | .0095 | .0000 | .0040 | .0070 | .0091 | .0108 | .0119 | .0127 | .0132 | .0133 |

Note: $\bar{C}$ is found by integrating over the film using Simpson's rule.

to solvent loss being just at the surface. Some of this same type effect is present in the second phase; the major resistance to solvent loss is just within the surface layer in this case, and a relatively free transport can occur within the film itself. This leads to relatively flat concentration profiles in the film as can be seen in Figure 7.5 and Table 7.2. These profiles are independent of B, meaning they are independent of first stage phenomena.

It is interesting to note how well $C_A$ corresponds to $M_\infty$. $D_0$ has been taken as $10^{-14}$ to plot the experimental evaporation data. Beyond the break in the curve, the experimental data lie below the calculated data because about 1 per cent

Table 7.3

Constants for the Mathematical Evaluation of Solvent Evaporation from Poly(vinyl Acetate) Films

| Solvent | $D_o$, cm²/sec. | $C_A$, vol. fract. | $V_2$, decades | B | $V_t$ |
|---|---|---|---|---|---|
| Methanol. . . . . . . . . . . . | $4.46 \times (10)^{-10}$ | 0.11 | 2.0 | $10^3$ | $3 \times (10)^4$ |
| Methyl cellosolve. . . . . | $1.78 \times (10)^{-12}$ | 0.145 | 3.8 | $6.3 \times (10)^4$ | $6.3 \times (10)^7$ |
| Chlorobenzene. . . . . . . | $1.0 \times (10)^{-11}$ | 0.20 | 6.0 | $10^6$ | $10^{10}$ |
| Cyclohexanone. . . . . . . | $1.0 \times (10)^{-14}$ | 0.25 | 6.0 | $10^6$ | $10^{10}$ |

Note: $D_o$ for cyclohexanone was increased from $2.5 \times (10)^{-15}$ to help account for the effect of water.

water is absorbed by the film. This water presumably penetrates into the film just after this point and starts its very strong plastizicing action. This essentially increases $D_0$ allowing a more rapid evaporation than that calculated from diffusion coefficient data obtained in water-free systems. The calculated curves fit some of the experimental evaporation curves for Vinylite VYHH and poly(ethyl methacrylate) better, since these polymers have negligible water absorption and comparable diffusion conditions.

## 7.6 *Further Calculations*

Calculations for the evaporation of chlorobenzene from poly(vinyl acetate) have shown that the mathematical model developed for describing the evaporation of solvent from a film is reasonable. Having measured diffusion coefficients for other solvents in poly(vinyl acetate), it would be natural to see what results can be obtained when these constants are put into the model. The constants chosen for this purpose are given in Table 7.3, and the results of the calculations are given in Figure 7.6. The corresponding concentration profiles for these cases are given in Table 7.4 and Figure 7.7. The agreement between the calculated and the measured drying curves is very good.

Figure 7.6 must be interpreted in the light of the values for $D_0$ in each case. The reduced time variable must not be confused with actual time. Actual time is plotted in Figure 5.7, modified by the square of the film thickness. Multiplying the $t/(L')^2$ values in Figure 5.7 by the corresponding $D_0$ values gives the curves indicated in Figure 7.6.

$C_A$ and $M_0$ are very close in each case. Increasing $C_A$ while keeping $V_2$ constant leads to greater solvent retention. This can be seen by a greater calculated retention for cyclohexanone than for chlorobenzene, and can probably be traced to a lower plasticizing effectiveness for cyclohexanone. Methanol is similarly retained less at $M_0$ than methyl cellosolve (EGMME). Increasing $V_2$ leads to flatter retention curves, similar to those of Vinylite VYHH. At the same time higher $V_2$ leads to slightly flatter concentration profiles in the interior of the film.

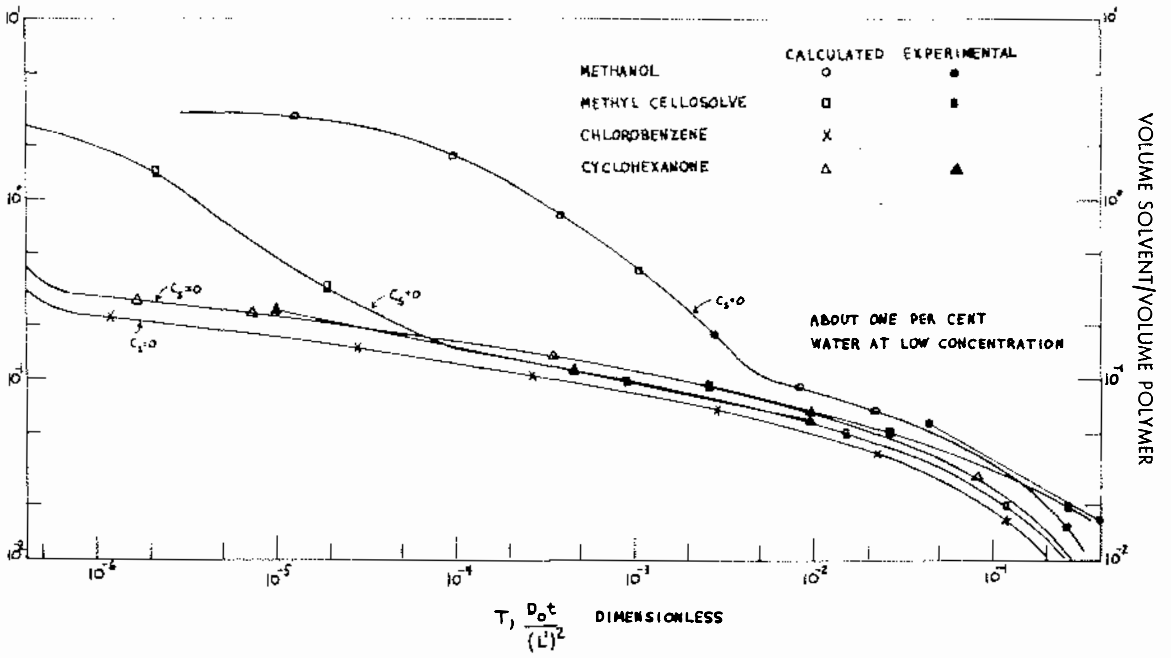


Figure 7.6. Calculated and experimental drying curves for the evaporation of various solvents from poly(vinyl acetate)

The concentration profiles found in these calculations are identical to those found in the calculations in Chapter 6. The concentration gradients reported in Appendix A.2 for desorption from a plane film can be used to estimate concentration gradients in the second phase. $V_2$ need only be taken as V and $C_A$ as the initial concentration.

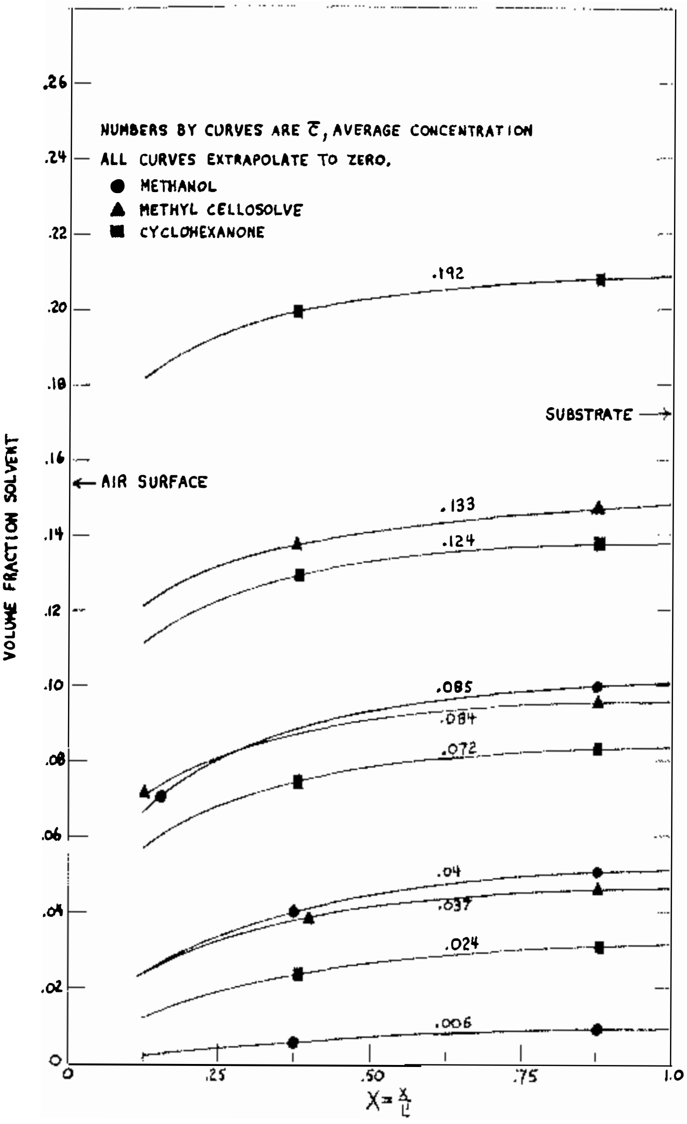


Figure 7.7. Calculated concentration gradients during the evaporation of various solvents from poly(vinyl acetate)

Table 7.4

Calculated Concentration Gradients for the Evaporation of Various Solvents from Poly(vinyl Acetate). Concentrations in Volume Fractions

|  | LOG T | $\bar{C}$ | X |  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  | 0 | 0.125 | 0.250 | 0.375 | 0.500 | 0.625 | 0.750 | 0.875 | 1.000 |
| Cyclohexanone | −6.184 | .2369 | .0462 | .2258 | .2371 | .2431 | .2468 | .2493 | .2539 | .2578 | .2591 |
|  | −5.286 | .1916 | .0000 | .1822 | .1935 | .1995 | .2032 | .2057 | .2072 | .2082 | .2084 |
|  | −4.363 | .1541 | .0000 | .1431 | .1544 | .1604 | .1641 | .1666 | .1682 | .1690 | 1.693 |
|  | −3.614 | .1241 | .0000 | .1118 | .1231 | .1291 | .1328 | .1353 | .1369 | .1377 | .1380 |
|  | −3.051 | .1017 | .0000 | .0884 | .0996 | .1056 | .1094 | .1118 | .1134 | .1143 | .1146 |
|  | −2.302 | .0719 | .0000 | .0576 | .0686 | .0745 | .0782 | .0807 | .0822 | .0831 | .0834 |
|  | −1.742 | .0500 | .0000 | .0358 | .0460 | .0516 | .0552 | .0576 | .0591 | .0599 | .0602 |
|  | −1.017 | .0237 | .0000 | .0127 | .0195 | .0238 | .0268 | .0288 | .0301 | .0309 | .0311 |
|  | −0.463 | .0082 | .0000 | .0031 | .0057 | .0076 | .0092 | .0103 | .0111 | .0116 | .0117 |
| Methyl cellosolve | −5.018 | .3112 | .0407 | .2320 | .2898 | .3206 | .3398 | .3525 | .3605 | .3651 | .3665 |
|  | −4.648 | .2204 | .0129 | .1436 | .1953 | .2260 | .2453 | .2579 | .2660 | .2705 | .2720 |
|  | −4.106 | .1326 | .0000 | .1216 | .1320 | .1375 | .1409 | .1432 | .1446 | .1472 | .1487 |
|  | −3.365 | .1047 | .0000 | .0930 | .1033 | .1088 | .1122 | .1145 | .1159 | .1167 | .1170 |
|  | −2.804 | .0841 | .0000 | .0716 | .0819 | .0873 | .0908 | .0930 | .0945 | .0953 | .0955 |
|  | −2.056 | .0570 | .0000 | .0438 | .0536 | .0590 | .0623 | .0646 | .0660 | .0668 | .0670 |
|  | −1.500 | .0374 | .0000 | .0248 | .0335 | .0384 | .0416 | .0437 | .0451 | .0458 | .0461 |
|  | −0.408 | .0064 | .0000 | .0024 | .0044 | .0060 | .0072 | .0081 | .0088 | .0092 | .0093 |
| Methanol | −2.120 | .0855 | .0000 | .0665 | .0808 | .0885 | .0934 | .0966 | .0986 | .0998 | .1002 |
|  | −1.748 | .0714 | .0000 | .0476 | .0610 | .0685 | .0732 | .0764 | .0784 | .0795 | .0799 |
|  | −1.200 | .0413 | .0000 | .0232 | .0338 | .0402 | .0444 | .0473 | .0491 | .0502 | .0505 |
|  | −0.652 | .0168 | .0000 | .0116 | .0190 | .0241 | .0278 | .0303 | .0320 | .0329 | .0333 |
|  | −0.285 | .0062 | .0000 | .0022 | .0041 | .0051 | .0070 | .0080 | .0087 | .0091 | .0092 |

Note: $\bar{C}$ is found by integrating over the film using Simpson's rule.

Increasing the plasticizer content of a film or increasing the temperature of drying increases $D_0$ and decreases $C_A$; $V_2$ is decreased. Solvent leaves the film more rapidly after being retained at a lower $M_0$. A plasticized, water-free film laid down from cyclohexanone could be described by the curve for chlorobenzene in Figure 7.6, for example.

Drying in the first phase is more rapid for an initial solvent concentration lower than the 0.75 volume fraction assumed here. Calculated curves showed that the first phase curve roughly parallels the given curves, and that second phase diffusion is unaffected by changing the initial solvent concentration.

If B is drastically reduced the second stage may become unrecognizable. Low B values will be found in the evaporation of plasticizers from films, or in the evaporation of solvents from very thin films. The evaporation of o-xylene from ethyl cellulose is another example.

### 7.7 *Conclusion*

The close correspondence between measured and calculated solvent evaporation curves demonstrates the validity of the fundamental concepts behind the mathematical model designed to simulate solvent evaporation. It is boundary layer resistance which controls solvent loss in the first phase, and internal diffusion resistance which controls loss in the second phase. The exponential concentration dependence of the solvent in polymer diffusion coefficient must be taken into consideration to properly understand the complete story of solvent evaporation.

## Chapter 8

# Discussion of Results

### 8.1 *Introduction*

This chapter is of a more diverse, speculative nature than the previous chapters. It includes numerous ideas and suggestions which have not been fully developed but which can give some insight into the phenomena involved or perhaps serve as a basis for further research. These ideas and observations have been grouped under the general areas listed below.

### 8.2 *Emulsifiers*

A more definitive study of the usefulness of the three dimensional solubility parameter concept to the solution of practical problems involving emulsifier selection appears very promising. The results found with use of the HLB system would indicate the solubility parameter can also be used to simplify choice of emulsifiers for specific applications (Weidner 1965, Pascal and Reig 1964). See Section 3.2.

### 8.3 *Pigment-Binder-Solvent Interactions*

It is possible to apply the solubility parameter to the interpretation of pigment-binder-solvent interactions, including problems in dispersion, binder adsorption, charge phenomena, and optimizing formulations. Computer programming of the results of such studies would lead to efficient solution of many problems. Work within this area is in progress, though the precise principles for selection of paint components have not been fully developed.

### 8.4 *Design of New Materials*

Natural products such as cellulose have been altered by adding groups, such as nitro or ethyl, onto the chain to improve solubility properties. Cellulose, with numerous rings and alcohol groups, must lie at high $\delta_d$, high $\delta_p$, and high $\delta_h$, perhaps somewhere in the neighborhood of its natural glue, lignin. Milled wood lignin (Björkman 1956) is located at about $\delta_d = 10.85$, $\delta_p = 7.0$, and $\delta_h = 8.8$ as can be seen in Figures 8.1, 8.2, and 8.3. Adding a group to the cellulose molecule moves the volume of solubility in a distinct direction. Similar predictions of the properties of new or modified materials can be made. This type of thinking is

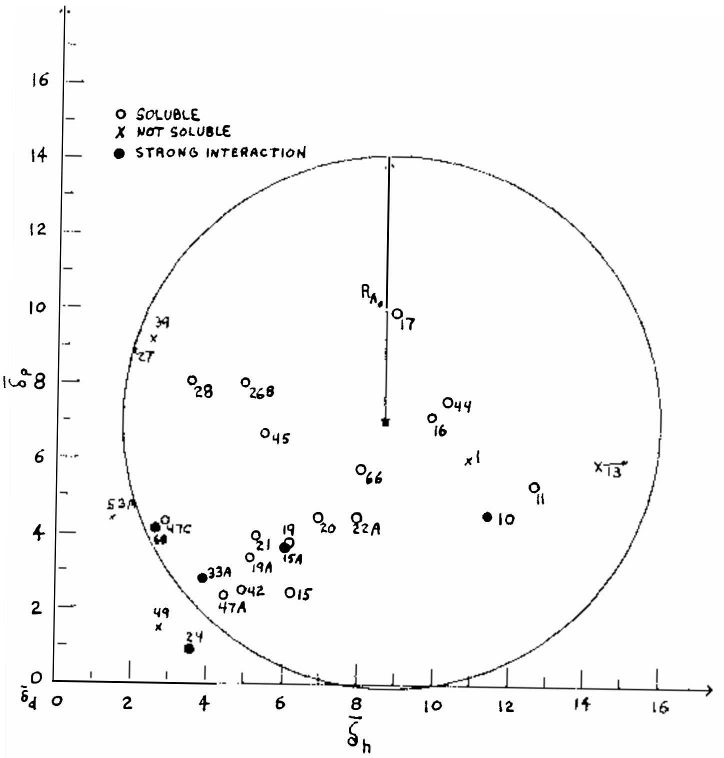


Figure 8.1. The solubility of milled wood lignin

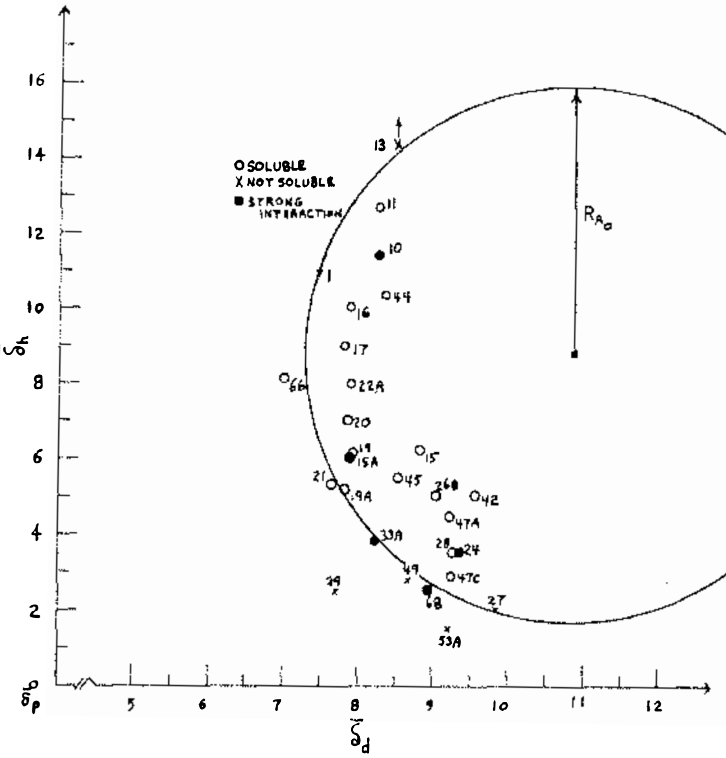


Figure 8.2. The solubility of milled wood lignin

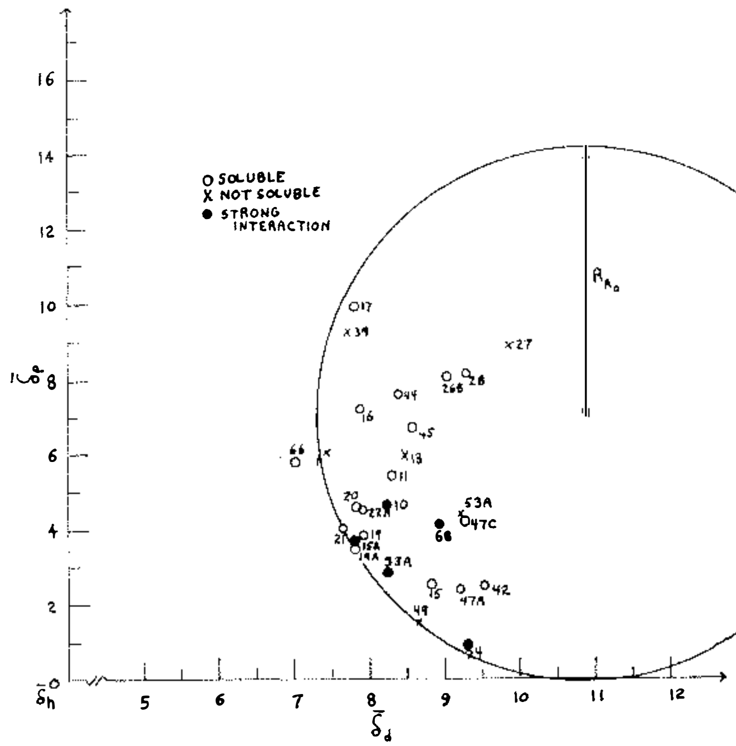


Figure 8.3. The solubility of milled wood lignin

valid for pigment surface treatment. Trends can even be seen in the swelling of the Sephadex® LH-20 type gels for gel filtration in organic solvents. Data for this swelling are given in Table 8.1. The swelling is largest in solvents having high $\delta_d$, $\delta_p$, and $\delta_h$.

A group contribution method to calculate the three components of the solubility parameter would be very helpful to predict the properties of new or modified materials. The effect of several groups of a different nature in the same molecule can lead to cancelling effects in some cases and reinforcing effects in others, however, so no serious attempts to do this have been made.

## 8.5 *Further Characterizations*

In view of the success of the three dimensional solubility parameter in predicting relations among materials of various types, it would seem natural to describe other materials in the same manner. Research as well as practical application can benefit from the characterization of more materials. Studies on a few well-chosen materials can be used to predict relationships in many materials. It would seem that manufacturers would characterize their products to help sell them by helping their customers to use them.

Table 8.1
Manufacturers Data for the Swelling of Sephadex® LH-20 (Pharmacia Fine Chemicals, Uppsala, Sweden)

| Solvent | Appr. solvent regain, ml solvent/g dry gel | Appr. bed volume ml/g dry gel |
|---|---|---|
| Dimethylformamide | 2.2 | 4 |
| Water | 2.1 | 4 |
| Methanol | 1.9 | 3.5–4.0 |
| Ethanol | 1.8 | 3.0–3.5 |
| Chloroform* | 1.8 | 3.0–3.5 |
| n-Butanol | 1.6 | 3 |
| Dioxane | 1.4 | 2.5–3.0 |
| Tetrahydrofurane | 1.4 | 2.5–3.0 |
| Acetone | 0.8 | 1.5 |
| Ethyl acetate | 0.4 | 0.5–1.0 |
| Toluene | 0.2 | 0.5 |

*) Containing 1 % ethanol. Particle size: 25–100 μ.

The solubility of many non-polymeric materials can also be discussed in terms of the three dimensional solubility parameter. The miscibility of solvents might be mentioned in this connection. The solubilities of such well-known materials as sulfur and urea can also be interpreted in terms of the three dimensional solubility parameter system. The primary room temperature solvent for sulfur is carbon disulfide; its nearest neighbors in the system become good solvents at higher temperatures. Urea ($\delta_{d_0} \approx 12$, $\delta_{p_0} \approx 10.5$, $\delta_{h_0} \approx 13.5$) dissolves in dimethyl formamide, dimethyl sulphoxide, and the solvents having a $\delta_h$ greater than 6.0 (with the exception of the cyclohexanol and the alcohol series greater in size than methanol). There even seems to be a relation between the placements of several of the solvents known to absorb rapidly in human skin, such as dimethyl sulphoxide, m-cresol, and the low molecular weight alcohols. It would appear that human skin could be characterized by solubility parameter values not too different from those of milled wood lignin.

The volumes of solubility are not spherical when plotting is done with equal unit distances for $\delta_d$, $\delta_p$, and $\delta_h$. If, however, the unit distance for $\delta_d$ is taken as twice that for $\delta_p$ and $\delta_h$, essentially spherical volumes of solubility are found. The dispersion interactions are fundamentally different from the polar and hydrogen bonding interactions, which are of a similar nature. The dispersion forces arise from atomic, induced dipole-induced dipole interactions, while the polar and hydrogen bonding forces arise from molecular, permanent dipole-permanent dipole interactions. Thus it is not surprising that the effect of dispersion forces is not exactly the same as that of the directed, permanent polar and hydrogen bonding forces. Since the interaction plots can be made spherical by the technique described above, an equation for the condition of solution (or interaction) can be written. Requiring the distance between a solute's center point and the point representing the solvent, $R_A$, be less than the distance between the center point and the boundary leads to:

8.2) $$R_A^2 = 4(\delta_{d1} - \delta_{d0})^2 + (\delta_{p1} - \delta_{p0})^2 + (\delta_{h1} - \delta_{h0})^2 < R_{A0}^2$$

Larger differences in $\delta_p$ and $\delta_h$ than in $\delta_d$ are allowed for solubility as is clearly shown by this method of plotting interaction data developed by Mr. Klemen Skaarup. A material can thus be characterized by the method described by four parameters: $\delta_{d0}$, $\delta_{p0}$, $\delta_{h0}$, and its interaction radius $R_{A0}$. For pigments these should perhaps be primed to indicate a surface property. Because of the very close relation between surface properties and bulk solvent properties, this important theoretical difference has no evident practical consequence.

## 8.6 *Solution Thermodynamics*

The purpose of a thermodynamic approach to the question of solubility would be to describe a method to calculate each of the factors entering the free energy equation.

8.1) $$\Delta F^M = \Delta H^M - T\Delta S^M$$

This appears impossible at the present time because the hydrogen bond energy and the hydrogen bond entropy are not independent of each other (Pimentel 1960). The entropy of hydrogen bond formation increases with the increased order associated with higher energies of hydrogen bond formation. This would increase the possibility of solution in more hydrogen bonded solvents since the heat and entropy terms in Equation 8.1 tend to cancel.

The similarity of the nature of the type interactions involved in polar bonding to those involved in hydrogen bonding would indicate a similar situation for both polar and hydrogen bonded solvents. $\delta_p$ and $\delta_h$ were, indeed, found from the same single quantity, the association parameter, $\delta_a$. Thus, larger differences in $\delta_p$ and $\delta_h$ are allowed than in $\delta_d$ for solution, since $\Delta H^M$ and $T\Delta S^M$ are not independent.

The mutual dependence of the enthalpy and entropy terms related to polar and hydrogen bonding energies in the free energy equation complicates matters in some respects. One would naturally suspect the entropy term could also be divided into components comparable to the enthalpy term. The individual evaluation of the two terms has not been found necessary, from a practical point of view, because of their interdependence. What has been evaluated by the experiments described here is a boundary or the state where solubility just occurs. This was done without specific regard to how solubility occurred. It was quite simply assumed that a similarity of the solubility parameters of the solvent and solute was necessary if solubility was found. This simple assumption has been sufficient to develop the system. An extension of the present approach to separate evaluations of $\Delta H$ and $T\Delta S$ will evidently be complicated by their interdependence. The question of finding the thermodynamic center for a given solute has not been settled since this also depends on the interdependence of $\Delta H^M$ and $T\Delta S^M$.

Additional information regarding the effect of temperature, molecular weight, and concentration can be gotten by referring to the Flory-Huggins equation for the free energy of mixing when a noncrystalline polymer is mixed with a solvent (Flory 1953). This equation includes a polymer-solvent interaction coefficient, $\chi$, which reflects the intermolecular forces between the molecules in solution.

8.3) $$\frac{\Delta G^M}{RT} = N_1 \ln \varnothing_1 + N_2 \ln \varnothing_2 + \chi \varnothing_1 \varnothing_2 (N_1 + m N_2)$$

where

$N_1$ = no. of moles of solvent
$N_2$ = no. of moles of polymer
m = ratio of molar volumes, polymer to solvent
$\varnothing_1 = N_1/(N_1 + mN_2)$
$\varnothing_2 = mN_2/(N_1 + mN_2)$

To reduce $\Delta G^M$, $\chi$ must be reduced as much as possible. A maximum value of $\chi$ can be found for the situation where there is solubility over the entire concentration range. This critical value, $\chi_c$, is given by

8.4) $$\chi_c = \tfrac{1}{2}\left(1 + \frac{1}{\sqrt{m}}\right)^2$$

For a polymer of infinite molecular weight, this value is 0.5. Thus $\chi$ is essentially 0.5 in a boundary region of solubility, and a slightly larger volume of solubility can be expected for decreasing molecular weights. The free energy of mixing $\Delta G^M$ is also essentially zero in the boundary; this should provide a basis for further work in the thermodynamic interpretations of the phenomena described here.

The effect of temperature, molecular weight, and concentration have more or less been indicated qualitatively in the foregoing chapters and in an article by the author (E). The size of the volumes of solubility increases for increasing temperature, decreasing concentration, and decreasing molecular weight. These effects have not been quantified, however. Concentration effects are more evident when more than one solute is present.

Sonnich Thomsen has related interesting solubility relations in terms of the solubility parameter. These situations involve examples including materials so varied in nature as gasses and diamond (Sonnich Thomsen 1966 A). He has also expanded the solubility parameter theory for calculating $\Delta E^M$ in non-polar liquids

(Sonnich Thomsen 1966 B). This approach of extensive calculations has not been found suitable for the present study which had the object of a very simple description of the materials involved and the relation of their properties to each other. There is no doubt that working with potential distribution functions is a necessary part of developing solution theory; perhaps the present work will provide some new clues for further improvement in the present state of solution theory.

It is significant that resort to the interpretation of hydrogen bonding in terms of acid and base pairing has not been necessary to explain any of close to 10,000 observations, many with mixed solvents. The cohesive energy density is fully sufficient to explain solubility relations in the organic systems studied.

## 8.7 *Surface Phenomena*

The characterization of pigments by the solubility parameter points toward a relation between the cohesive energy density and surface energy. The simple relation surface times distance equals volume indicates a relation between the surface tension, γ, and the solubility parameter should be of the form

$$\gamma\left(\frac{\text{energy}}{\text{cm}^2}\right) \alpha \left[\delta^2\left(\frac{\text{energy}}{\text{cm}^3}\right) \times V_m^{\frac{1}{3}}\,(\text{cm})\right]$$

Klemen Skaarup has indeed found such a relation for the surface tension of pure liquids, (unpublished). The correlation involves γ and both $\delta_d$ and $\delta_a$. Since the energy of evaporation of a single, pure liquid is fully accounted for in these parameters, the surface tension is also. $\delta_a$ is sufficient to account for a liquid's association interactions with itself. Steric factors play a special role in surface phenomena. This same type correlation with δ would be different for surface energies at a completely different surface from air. Three dimensions would be expected in such a correlation. $\delta_a$ would have to be split into components as demonstrated by the three dimensional characterization of surface energy in the pigment suspension data.

The dispersion contribution to surface tension has been discussed in the recent literature in surface chemistry (Fowkes 1965). This topic is far too large to be discussed here, other than to indicate the perspectives involved, though it is significant that the division of the total energies involved into components has also been considered in other fields.

The critical surface tension, $\gamma_c$, of a solid surface is a measure of its wetting properties (Zisman 1964). Any solid surface with $\gamma_c$ equal to or larger than the γ of a liquid will be spread upon by that liquid. Some authorities warn against indiscriminate use of this concept (Fowkes 1965, Sharpe and Schonhorn 1964) though its usefulness can not be denied. The author also has an observation regarding several of the polymeric materials characterized by $\gamma_c$ (Zisman 1964). In Table 8.2 are listed a number of solvents which actually dissolve the polymers

Table 8.2
A Comparison of the Critical Surface Tension of Polymers and the Surface Tensions of Several Solvents which Dissolve them. $\gamma_c$ from (Zisman 1964)

| Poly(methyl methacrylate)<br>$\gamma_c = 39$ | Poly(styrene)<br>$\gamma_c = 33$ | Poly(vinyl chloride)<br>$\gamma_c = 39$ |
|---|---|---|
| Acetophenone (39.8)<br>Benzaldehyde (40)<br>Propylene carbonate (40.5)<br>Nitrobenzene (43.9) | Pyridine (38.0)<br>Acetophenone (39.8)<br>Benzaldehyde (40)<br>Nitrobenzene (43.9)<br>Aniline (44.1) | Benzaldehyde (40) |

while the critical surface tension concept indicates they should not wet them. This would seem to be in conflict with the theory.

It could be that these particular substrates should be considered as supercooled liquids rather than as solids. Crystallinity may also be a factor in proper interpretation of the situation. The solvents given in Table 8.2 all have high $\delta_d$.

$\gamma_c$ has been related to adhesion (Weiss 1964), and the probability that a relation exists between the solubility parameter and $\gamma_c$ has been indicated (Gardon 1963). One concludes on the basis of all this evidence and the adsorption of solvents on pigments that there must also exist a relation between the three dimensional parameter and adhesion phenomena.

The author has also been interested in the first event which occurs when a polymeric solute presents its surface to a solvent. Solution involves diffusion through this surface and subsequent transport of the solute away from it. The solution process is thus dependent on a critical attraction between solvent and solute at a surface, and later on the diffusional phenomena leading to a uniform mixture.

## 8.8 *Solvent Retention*

Solvent retention has been studied rather extensively in simple systems to clarify the effect of the various factors involved. Enlarging the scope of this work to solvent mixtures, the effect of various pigments, and to studies on azeotropic systems would be a logical, practical extension of the previous work. The effect of retained solvent could also be studied by tensile testing, rather than with the torsion pendulum.

Generalization of diffusion coefficients by a group contribution method would be a theoretically sound method of approaching the solvent retention problem. The measurement of retained solvent by the method developed by the author does in fact indirectly do this, however, and has the advantage of showing directly the amount of solvent retained at a given time for an arbitrary film thickness. Diffusion coefficients should be measured for a »theoretically correct« approach.

It has been noted that Vinylite VYHH films browned when oven treated at 95° C if they contained methyl isoamyl ketone or methyl isobutyl ketone. This was not the case with films made from methyl ethyl ketone even after prolonged heating. This would indicate a relation between heat stability and the amount of retained solvent may exist. Methyl ethyl ketone is retained to a lesser degree than the other, larger ketones.

## 8.9 *Conclusion*

It is hoped that the material covered in this volume will be useful to those who have problems within its scope. Likewise it is hoped that this study will stimulate interest to such a degree that others will also begin working within the same areas. In this respect the author is always interested in what others might eventually do with these ideas. Time has a way of changing things, so the three dimensional solubility parameter may not be here to stay, but it is going to be around for a while, and whatever the future will hold will certainly be related to it.

## Appendix A.1

## Concentration Gradients for Absorption in a Plane Film for Exponential Diffusion Coefficients, 16 Intervals

| V | LOG T | $\bar{C}$ | .125 | .250 | .375 | .500 | .625 | .750 | .875 | 1.000 |
|---|---|---|---|---|---|---|---|---|---|---|
| $10^1$ | −3.408 | .0516 | .0250 | .0001 | .0000 | .0000 | .0000 | .0000 | .0000 | .0000 |
| | −2.709 | .1125 | .4256 | .0119 | .0001 | .0000 | .0000 | .0000 | .0000 | .0000 |
| | −2.107 | .2225 | .7791 | .4319 | .0792 | .0045 | .0002 | .0000 | .0000 | .0000 |
| | −1.745 | .3365 | .8655 | .6843 | .4412 | .1742 | .0323 | .0036 | .0003 | .0000 |
| | −1.563 | .4148 | .8939 | .7595 | .5871 | .3743 | .1620 | .0411 | .0071 | .0019 |
| | −1.383 | .5101 | .9157 | .8137 | .6891 | .5372 | .3602 | .1855 | .0692 | .0337 |
| | −1.204 | .6265 | .9327 | .8543 | .7625 | .6548 | .5304 | .3953 | .2754 | .2238 |
| | −1.026 | .7661 | .9492 | .8928 | .8308 | .7640 | .6956 | .6321 | .5849 | .5671 |
| | −0.849 | .9040 | .9742 | .9477 | .9212 | .8961 | .8738 | .8562 | .8447 | .8408 |
| | −0.673 | .9809 | .9943 | .9888 | .9836 | .9789 | .9751 | .9722 | .9704 | .9698 |
| $10^2$ | −4.407 | .0401 | .0020 | .0000 | .0000 | .0000 | .0000 | .0000 | .0000 | .0000 |
| | −3.709 | .0946 | .1550 | .0000 | .0000 | .0000 | .0000 | .0000 | .0000 | .0000 |
| | −2.976 | .2032 | .8349 | .2832 | .0007 | .0000 | .0000 | .0000 | .0000 | .0000 |
| | −2.615 | .3051 | .9039 | .7418 | .3089 | .0025 | .0000 | .0000 | .0000 | .0000 |
| | −2.435 | .3762 | .9251 | .8148 | .6184 | .1317 | .0009 | .0000 | .0000 | .0000 |
| | −2.256 | .4615 | .9411 | .8618 | .7447 | .5364 | .0956 | .0010 | .0000 | .0000 |
| | −2.077 | .5658 | .9532 | .8942 | .8161 | .7034 | .5140 | .1380 | .0030 | .0001 |
| | −1.900 | .6933 | .9626 | .9178 | .8624 | .7909 | .6925 | .5412 | .2676 | .0388 |
| | −1.723 | .8491 | .9712 | .9383 | .9007 | .8576 | .8091 | .7578 | .7133 | .6944 |
| | −1.546 | .9757 | .9930 | .9860 | .9794 | .9733 | .9681 | .9641 | .9616 | .9608 |
| | −1.370 | .9992 | .9997 | .9995 | .9993 | .9991 | .9989 | .9988 | .9987 | .9987 |
| $10^3$ | −5.407 | .0340 | .0001 | .0000 | .0000 | .0000 | .0000 | .0000 | .0000 | .0000 |
| | −4.708 | .0826 | .0256 | .0000 | .0000 | .0000 | .0000 | .0000 | .0000 | .0000 |
| | −3.916 | .1863 | .8521 | .0309 | .0000 | .0000 | .0000 | .0000 | .0000 | .0000 |
| | −3.556 | .2749 | .9225 | .7592 | .0094 | .0000 | .0000 | .0000 | .0000 | .0000 |
| | −3.201 | .4144 | .9522 | .8822 | .7560 | .1418 | .0000 | .0000 | .0000 | .0000 |
| | −3.024 | .5069 | .9624 | .9121 | .8372 | .6940 | .0655 | .0000 | .0000 | .0000 |
| | −2.847 | .6201 | .9701 | .9325 | .8828 | .8100 | .6781 | .1177 | .0000 | .0000 |
| | −2.670 | .7554 | .9760 | .9475 | .9122 | .8667 | .8031 | .6985 | .3924 | .0017 |
| | −2.493 | .9244 | .9835 | .9652 | .9452 | .9237 | .9017 | .8813 | .8661 | .8604 |
| | −2.317 | .9978 | .9993 | .9987 | .9981 | .9976 | .9971 | .9968 | .9966 | .9965 |
| $10^4$ | −6.407 | .0308 | .0000 | .0000 | .0000 | .0000 | .0000 | .0000 | .0000 | .0000 |
| | −5.504 | .0938 | .0401 | .0000 | .0000 | .0000 | .0000 | .0000 | .0000 | .0000 |
| | −4.916 | .1578 | .8760 | .0003 | .0000 | .0000 | .0000 | .0000 | .0000 | .0000 |
| | −4.556 | .2371 | .9257 | .5964 | .0000 | .0000 | .0000 | .0000 | .0000 | .0000 |
| | −4.201 | .3559 | .9565 | .8844 | .6690 | .0000 | .0000 | .0000 | .0000 | .0000 |
| | −4.024 | .4435 | .9665 | .9186 | .8370 | .2777 | .0000 | .0000 | .0000 | .0000 |
| | −3.846 | .5449 | .9732 | .9378 | .8867 | .7969 | .1511 | .0000 | .0000 | .0000 |
| | −3.670 | .6642 | .9787 | .9524 | .9181 | .8694 | .7868 | .2720 | .0000 | .0000 |
| | −3.493 | .8081 | .9829 | .9627 | .9381 | .9066 | .8632 | .7946 | .6369 | .0006 |
| | −3.317 | .9764 | .9936 | .9871 | .9806 | .9744 | .9690 | .9646 | .9618 | .9609 |

Appendix A.1 (continued)

| V | LOG T | $\bar{C}$ | .125 | .250 | .375 | .500 | .625 | .750 | .875 | 1.000 |
|---|---|---|---|---|---|---|---|---|---|---|
| $10^5$ | −7.407 | .0288 | .0000 | .0000 | .0000 | .0000 | .0000 | .0000 | .0000 | .0000 |
| | −6.708 | .0605 | .0002 | .0000 | .0000 | .0000 | .0000 | .0000 | .0000 | .0000 |
| | −6.328 | .1022 | .0927 | .0000 | .0000 | .0000 | .0000 | .0000 | .0000 | .0000 |
| | −5.794 | .1637 | .7364 | .0000 | .0000 | .0000 | .0000 | .0000 | .0000 | .0000 |
| | −5.434 | .2442 | .9407 | .6836 | .0000 | .0000 | .0000 | .0000 | .0000 | .0000 |
| | −5.255 | .3105 | .9559 | .8637 | .0095 | .0000 | .0000 | .0000 | .0000 | .0000 |
| | −4.900 | .4588 | .9742 | .9377 | .8756 | .3793 | .0000 | .0000 | .0000 | .0000 |
| | −4.723 | .5646 | .9793 | .9522 | .9138 | .8485 | .2317 | .0000 | .0000 | .0000 |
| | −4.546 | .6873 | .9835 | .9632 | .9370 | .9002 | .8378 | .3948 | .0000 | .0000 |
| | −4.370 | .8388 | .9867 | .9710 | .9519 | .9278 | .8952 | .8453 | .7400 | .0002 |
| | −4.193 | .9928 | .9979 | .9958 | .9939 | .9921 | .9906 | .9895 | .9888 | .9885 |
| $10^6$ | −8.407 | .0275 | .0000 | .0000 | .0000 | .0000 | .0000 | .0000 | .0000 | .0000 |
| | −7.504 | .0737 | .0005 | .0000 | .0000 | .0000 | .0000 | .0000 | .0000 | .0000 |
| | −6.945 | .1260 | .6219 | .0000 | .0000 | .0000 | .0000 | .0000 | .0000 | .0000 |
| | −6.581 | .1997 | .9221 | .0043 | .0000 | .0000 | .0000 | .0000 | .0000 | .0000 |
| | −6.225 | .2891 | .9627 | .8827 | .0001 | .0000 | .0000 | .0000 | .0000 | .0000 |
| | −6.047 | .3537 | .9705 | .9201 | .4855 | .0000 | .0000 | .0000 | .0000 | .0000 |
| | −5.871 | .4414 | .9759 | .9400 | .8699 | .0317 | .0000 | .0000 | .0000 | .0000 |
| | −5.694 | .5346 | .9816 | .9570 | .9196 | .8398 | .0009 | .0000 | .0000 | .0000 |
| | −5.517 | .6549 | .9853 | .9669 | .9422 | .9048 | .8255 | .0022 | .0000 | .0000 |
| | −5.341 | .8017 | .9881 | .9739 | .9564 | .9336 | .9014 | .8465 | .1856 | .0000 |
| | −5.165 | .9725 | .9934 | .9862 | .9787 | .9711 | .9639 | .9578 | .9536 | .9521 |
| $10^7$ | −9.407 | .0256 | 0.000 | .0000 | .0000 | .0000 | .0000 | .0000 | .0000 | .0000 |
| | −8.504 | .0662 | .0000 | .0000 | .0000 | .0000 | .0000 | .0000 | .0000 | .0000 |
| | −8.106 | .1082 | .1827 | .0000 | .0000 | .0000 | .0000 | .0000 | .0000 | .0000 |
| | −7.562 | .1860 | .9319 | .0001 | .0000 | .0000 | .0000 | .0000 | .0000 | .0000 |
| | −7.203 | .2713 | .9662 | .8935 | .0000 | .0000 | .0000 | .0000 | .0000 | .0000 |
| | −7.025 | .3438 | .9737 | .9284 | .1948 | .0000 | .0000 | .0000 | .0000 | .0000 |
| | −6.848 | .4144 | .9790 | .9471 | .8786 | .0001 | .0000 | .0000 | .0000 | .0000 |
| | −6.671 | .5008 | .9829 | .9594 | .9231 | .8447 | .0000 | .0000 | .0000 | .0000 |
| | −6.495 | .6140 | .9863 | .9689 | .9448 | .9069 | .8211 | .0000 | .0000 | .0000 |
| | −6.319 | .7586 | .9893 | .9764 | .9603 | .9387 | .9060 | .8366 | .0000 | .0000 |
| | −6.142 | .9328 | .9914 | .9813 | .9694 | .9548 | .9360 | .9095 | .8648 | .5522 |
| $10^8$ | −10.41 | .0258 | .0000 | .0000 | .0000 | .0000 | .0000 | .0000 | .0000 | .0000 |
| | −9.503 | .0605 | .0000 | .0000 | .0000 | .0000 | .0000 | .0000 | .0000 | .0000 |
| | −8.944 | .1157 | .3509 | .0000 | .0000 | .0000 | .0000 | .0000 | .0000 | .0000 |
| | −8.581 | .1664 | .9403 | .0000 | .0000 | .0000 | .0000 | .0000 | .0000 | .0000 |
| | −8.225 | .2483 | .9624 | .6773 | .0000 | .0000 | .0000 | .0000 | .0000 | .0000 |
| | −8.047 | .3133 | .9723 | .9127 | .0003 | .0000 | .0000 | .0000 | .0000 | .0000 |
| | −7.870 | .3719 | .9781 | .9410 | .7780 | .0000 | .0000 | .0000 | .0000 | .0000 |
| | −7.673 | .4673 | .9840 | .9613 | .9226 | .2562 | .0000 | .0000 | .0000 | .0000 |
| | −7.517 | .5744 | .9867 | .9691 | .9436 | .8986 | .0720 | .0000 | .0000 | .0000 |
| | −7.341 | .6994 | .9896 | .9767 | .9600 | .9364 | .8964 | .1803 | .0000 | .0000 |
| | −7.164 | .8436 | .9916 | .9817 | .9695 | .9538 | .9318 | .8946 | .7313 | .0000 |
| | −6.988 | .9983 | .9995 | .9990 | .9985 | .9981 | .9978 | .9975 | .9974 | .9973 |

## Appendix A.2

## Concentration Gradients for Desorption in a Plane Film for Exponential Diffusion Coefficients

32 Intervals

| V | LOG T | $\bar{C}$ | X | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | .03125 | .0625 | .125 | .250 | .375 | .500 | .750 | 1.00 |
| $10^1$ | −2.217 | .8561 | .2663 | .4243 | .6159 | .8092 | .9032 | .9526 | .9908 | .9976 |
| | −1.684 | .7344 | .1642 | .2814 | .4439 | .6359 | .7504 | .8236 | .9031 | .9260 |
| | −1.330 | .6037 | .1110 | .1985 | .3303 | .5013 | .6088 | .6811 | .7625 | .7867 |
| | −1.154 | .5217 | .0860 | .1572 | .2695 | .4225 | .5222 | .5905 | .6685 | .6918 |
| | −0.978 | .4314 | .0630 | .1176 | .2079 | .3384 | .4272 | .4896 | .5621 | .5840 |
| | 0.801 | .3376 | .0432 | .0823 | .1501 | .2545 | .3294 | .3838 | .4484 | .4682 |
| | 0.625 | .2464 | .0277 | .0535 | .1004 | .1772 | .2358 | .2799 | .3340 | .3510 |
| | −0.448 | .1634 | .0162 | .0318 | .0610 | .1117 | .1527 | .1850 | .2261 | .2394 |
| | −0.272 | .0950 | .0085 | .0168 | .0328 | .0618 | .0867 | .1070 | .1340 | .1429 |
| | −0.096 | .0454 | .0038 | .0075 | .0147 | .0284 | .0405 | .0508 | .0649 | .0697 |
| | −0.081 | .0160 | .0013 | .0025 | .0050 | .0098 | .0141 | .0179 | .0232 | .0250 |
| $10^2$ | −3.217 | .9121 | .5205 | .6535 | .7826 | .8962 | .9481 | .9748 | .9951 | .9987 |
| | −2.507 | .8036 | .3684 | .4951 | .6273 | .7563 | .8254 | .8687 | .9150 | .9284 |
| | −2.153 | .7093 | .2871 | .4043 | .5315 | .6589 | .7283 | .7722 | .8196 | .8333 |
| | −1.800 | .5869 | .1973 | .2972 | .4134 | .5348 | .6023 | .6453 | .6920 | .7056 |
| | −1.447 | .4482 | .1157 | .1897 | .2859 | .3949 | .4581 | .4990 | .5441 | .5573 |
| | 1.271 | .3773 | .0831 | .1424 | .2250 | .3242 | .3837 | .4228 | .4663 | .4791 |
| | −1.094 | .3075 | .0572 | .1020 | .1692 | .2559 | .3102 | .3468 | .3880 | .4003 |
| | −0.918 | .2410 | .0377 | .0695 | .1208 | .1925 | .2401 | .2731 | .3110 | .3224 |
| | −0.742 | .1791 | .0236 | .0448 | .0811 | .1363 | .1754 | .2036 | .2368 | .2470 |
| | −0.566 | .1242 | .0140 | .0270 | .0507 | .0894 | .1189 | .1411 | .1682 | .1768 |
| | −0.390 | .0779 | .0076 | .0150 | .0288 | .0530 | .0726 | .0881 | .1080 | .1144 |
| | −0.213 | .0422 | .0037 | .0074 | .0144 | .0273 | .0384 | .0475 | .0597 | .0638 |
| | −0.037 | .0184 | .0015 | .0030 | .0060 | .0114 | .0163 | .0205 | .0264 | .0284 |
| $10^3$ | −4.176 | .9343 | .6642 | .7585 | .8477 | .9257 | .9617 | .9806 | .9958 | .9987 |
| | −3.287 | .8257 | .5164 | .6124 | .7069 | .7966 | .8443 | .8741 | .9061 | .9154 |
| | −2.757 | .7021 | .3953 | .4887 | .5820 | .6713 | .7190 | .7489 | .7810 | .7904 |
| | 2.403 | .6015 | .3012 | .3903 | .4814 | .5695 | .6168 | .6466 | .6787 | .6879 |
| | −2.050 | .4943 | .2085 | .2890 | .3752 | .4610 | .5075 | .5369 | .5687 | .5779 |
| | −1.697 | .3858 | .1279 | .1936 | .2704 | .3510 | .3958 | .4244 | .4556 | .4646 |
| | −1.343 | .2801 | .0680 | .1135 | .1742 | .2445 | .2858 | .3127 | .3423 | .3510 |
| | −0.990 | .1822 | .0310 | .0564 | .0958 | .1487 | .1828 | .2060 | .2325 | .2404 |
| | −0.814 | .1381 | .0197 | .0369 | .0657 | .1076 | .1365 | .1568 | .1806 | .1878 |
| | −0.462 | .0645 | .0067 | .0131 | .0249 | .0449 | .0608 | .0731 | .0885 | .0934 |
| | −0.285 | .0373 | .0034 | .0068 | .0131 | .0246 | .0342 | .0420 | .0523 | .0557 |
| | −0.109 | .0179 | .0015 | .0030 | .0059 | .0113 | .0161 | .0201 | .0256 | .0275 |
| $10^4$ | 4.997 | .9376 | .7258 | .7977 | .8664 | .9282 | .9585 | .9758 | .9920 | .9960 |
| | 4.110 | .8390 | .6068 | .6802 | .7517 | .8194 | .8554 | .8779 | .9021 | .9091 |
| | 3.580 | .7363 | .5034 | .5765 | .6479 | .7165 | .7515 | .7740 | .7983 | .8053 |
| | 3.051 | .6165 | .3832 | .4551 | .5261 | .5935 | .6294 | .6519 | .6761 | .6831 |
| | 2.522 | .4885 | .2604 | .3291 | .3984 | .4650 | .5006 | .5230 | .5471 | .5541 |
| | 2.168 | .4031 | .1834 | .2468 | .3133 | .3785 | .4136 | .4358 | .4598 | .4667 |
| | 1.816 | .3190 | .1165 | .1704 | .2311 | .2933 | .3275 | .3492 | .3728 | .3796 |
| | 1.286 | .1982 | .0456 | .0773 | .1205 | .1716 | .2019 | .2218 | .2437 | .2502 |
| | 0.933 | .1257 | .0202 | .0371 | .0640 | .1011 | .1255 | .1424 | .1616 | .1674 |
| | 0.580 | .0650 | .0075 | .0144 | .0269 | .0471 | .0624 | .0739 | .0879 | .0923 |
| | 0.403 | .0411 | .0041 | .0080 | .0153 | .0281 | .0384 | .0465 | .0568 | .0601 |
| | 0.227 | .0226 | .0020 | .0040 | .0077 | .0146 | .0205 | .0254 | .0318 | .0340 |
| | −0.051 | .0100 | .0008 | .0016 | .0032 | .0062 | .0089 | .0112 | .0144 | .0155 |

Appendix A.2. (continued)

| V | LOG T | $\bar{C}$ | X | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | .03125 | .0625 | .125 | .250 | .375 | .500 | .750 | 1.00 |
| $10^5$ | −6.038 | .9501 | .7845 | .8420 | .8967 | .9456 | .9693 | .9826 | .9947 | .9976 |
| | −4.977 | .8506 | .6665 | .7252 | .7826 | .8368 | .8656 | .8836 | .9030 | .9086 |
| | −4.271 | .7314 | .5461 | .6048 | .6621 | .7163 | .7451 | .7631 | .7825 | .7881 |
| | −3.742 | .6307 | .4446 | .5032 | .5604 | .6146 | .6434 | .6614 | .6808 | .6864 |
| | −3.211 | .5271 | .3409 | .3989 | .4559 | .5099 | .5386 | .5566 | .5760 | .5816 |
| | −2.681 | .4231 | .2389 | .2950 | .3510 | .4046 | .4332 | .4512 | .4705 | .4761 |
| | −2.152 | .3198 | .1444 | .1950 | .2480 | .3001 | .3282 | .3460 | .3651 | .3706 |
| | −1.623 | .2193 | .0689 | .1062 | .1508 | .1982 | .2249 | .2419 | .2604 | .2659 |
| | −1.270 | .1558 | .0353 | .0601 | .0941 | .1345 | .1586 | .1744 | .1919 | .1971 |
| | −0.917 | .0982 | .0155 | .0286 | .0496 | .0787 | .0980 | .1113 | .1266 | .1311 |
| | −0.565 | .0502 | .0057 | .0110 | .0205 | .0362 | .0481 | .0570 | .0680 | .0714 |
| | −0.388 | .0314 | .0031 | .0061 | .0116 | .0214 | .0293 | .0355 | .0435 | .0461 |
| | −0.212 | .0170 | .0015 | .0032 | .0058 | .0110 | .0154 | .0191 | .0240 | .0256 |
| $10^6$ | −7.038 | .9567 | .8204 | .8683 | .9139 | .9547 | .9744 | .9855 | .9956 | .9980 |
| | −5.800 | .8512 | .6992 | .7482 | .7960 | .8412 | .8652 | .8802 | .8964 | .9010 |
| | −5.094 | .7469 | .5938 | .6428 | .6906 | .7357 | .7597 | .7748 | .7909 | .7956 |
| | −4.388 | .6330 | .4788 | .5277 | .5755 | .6207 | .6447 | .6597 | .6758 | .6805 |
| | −3.858 | .5462 | .3912 | .4400 | .4878 | .5329 | .5569 | .5719 | .5881 | .5927 |
| | −3.152 | .4299 | .2748 | .3230 | .3704 | .4154 | .4394 | .4544 | .4705 | .4752 |
| | −2.623 | .3431 | .1901 | .2365 | .2831 | .3276 | .3514 | .3664 | .3825 | .3871 |
| | −2.094 | .2571 | .1124 | .1537 | .1974 | .2406 | .2639 | .2787 | .2946 | .2992 |
| | −1.565 | .1737 | .0519 | .0814 | .1173 | .1561 | .1781 | .1922 | .2075 | .2120 |
| | −1.035 | .0972 | .0174 | .0312 | .0524 | .0802 | .0979 | .1098 | .1233 | .1273 |
| | −0.683 | .0541 | .0068 | .0130 | .0238 | .0405 | .0526 | .0615 | .0720 | .0753 |
| | −0.506 | .0362 | .0039 | .0076 | .0143 | .0256 | .0344 | .0411 | .0495 | .0521 |
| | −0.329 | .0217 | .0021 | .0040 | .0078 | .0145 | .0201 | .0245 | .0303 | .0322 |
| | −0.153 | .0110 | .0009 | .0019 | .0037 | .0070 | .0100 | .0124 | .0157 | .0168 |
| $10^7$ | −8.038 | .9614 | .8461 | .8871 | .9262 | .9611 | .9780 | .9876 | .9962 | .9983 |
| | −6.623 | .8501 | .7211 | .7631 | .8041 | .8428 | .8634 | .8762 | .8901 | .8941 |
| | −5.918 | .7576 | .6276 | .6696 | .7105 | .7493 | .7698 | .7827 | .7965 | .8005 |
| | −5.034 | .6343 | .5030 | .5450 | .5860 | .6247 | .6453 | .6581 | .6720 | .6760 |
| | −4.328 | .5346 | .4024 | .4443 | .4853 | .5240 | .5446 | .5574 | .5713 | .5753 |
| | −3.622 | .4349 | .3019 | .3437 | .3846 | .4232 | .4438 | .4566 | .4705 | .4745 |
| | −2.917 | .3354 | .2029 | .2437 | .2842 | .3226 | .3431 | .3559 | .3698 | .3738 |
| | −2.211 | .2366 | .1102 | .1470 | .1852 | .2226 | .2428 | .2555 | .2692 | .2731 |
| | −1.858 | .1881 | .0708 | .1025 | .1377 | .1735 | .1931 | .2056 | .2191 | .2230 |
| | −1.328 | .1186 | .0285 | .0477 | .0734 | .1034 | .1210 | .1324 | .1451 | .1488 |
| | −0.975 | .0766 | .0129 | .0234 | .0399 | .0623 | .0767 | .0866 | .0979 | .1013 |
| | −0.623 | .0409 | .0049 | .0094 | .0173 | .0300 | .0395 | .0465 | .0549 | .0575 |
| | −0.446 | .0265 | .0027 | .0053 | .0101 | .0184 | .0250 | .0301 | .0365 | .0386 |
| | −0.270 | .0151 | .0014 | .0027 | .0053 | .0099 | .0139 | .0171 | .0213 | .0266 |
| $10^8$ | −8.657 | .9500 | .8421 | .8786 | .9140 | .9642 | .9470 | .9748 | .9859 | .9891 |
| | −7.420 | .8452 | .7334 | .7701 | .8060 | .8399 | .8579 | .8691 | .8812 | .8848 |
| | −6.537 | .7405 | .6276 | .6643 | .7002 | .7341 | .7520 | .7633 | .7754 | .7789 |
| | −5.655 | .6319 | .5178 | .5546 | .5904 | .6243 | .6423 | .6536 | .6657 | .6692 |
| | −4.772 | .5228 | .4076 | .4443 | .4802 | .5140 | .5320 | .5433 | .5554 | .5589 |
| | −3.890 | .4137 | .2975 | .3341 | .3699 | .4038 | .4218 | .4330 | .4452 | .4487 |
| | −3.008 | .3047 | .1886 | .2245 | .2600 | .2937 | .3116 | .3229 | .3350 | .3385 |
| | −2.303 | .2182 | .1063 | .1393 | .1732 | .2061 | .2238 | .2350 | .2470 | .2504 |
| | −1.598 | .1341 | .0412 | .0640 | .0915 | .1210 | .1375 | .1481 | .1597 | .1631 |
| | −1.069 | .0763 | .0141 | .0252 | .0418 | .0634 | .0769 | .0860 | .0963 | .0994 |
| | −0.716 | .0433 | .0056 | .0107 | .0194 | .0328 | .0423 | .0492 | .0574 | .0599 |
| | −0.539 | .0295 | .0033 | .0063 | .0119 | .0211 | .0282 | .0335 | .0401 | .0422 |
| | −0.363 | .0181 | .0018 | .0034 | .0066 | .0123 | .0169 | .0205 | .0252 | .0267 |

## Appendix A.3

## Viscosities and Specific Gravities for Solvents at 20° C

| | Viscosity Cp. | Specific gravity |
|---|---|---|
| 1 Methanol | 0.59 | 0.79 |
| 3 Ethanol 99.9 % | 1.22 | 0.82 |
| 4 n-Propanol | 2.26 | 0.81 |
| 5 n-Butanol | 2.96 | 0.81 |
| 6 Pentanol-1 | 4.00[a] | 0.81 |
| 7 2-Ethyl butanol | 5.63 | 0.83 |
| 8 2-Ethyl hexanol | 10.0 | 0.83 |
| 9 Methyl isobutyl carbinol | 5.18 | 0.81 |
| 10 Propylene glycol | 56.0 | 1.04 |
| 11 Ethylene glycol | 20.9 | 1.12 |
| 12 1,3 Butanediol | 104.0 | 1.01 |
| 13 Glycerol | 1410[b] | 1.25 |
| 14 Cyclohexanol | 20.3[c] | 0.95 |
| 15 m-Cresol | 18.4 | 1.03 |
| 15A Ethyl lactate | | 1.03 |
| 15B n-Butyl lactate | | 0.97 |
| 16 Diethylene glycol | 35.7 | 1.12 |
| 17 Dipropylene glycol | 107 | 1.03 |
| 18 2-Butoxyethanol | 6.42 | 0.90 |
| 19 Methyl dioxitol | 3.8 | 1.02 |
| 19A Butyl dioxitol | 6.8 | 0.96 |
| 20 Oxitol (Cellosolve) | 2.05 | 0.93 |
| 21 Diacetone alcohol | 3.2 | 0.94 |
| 22 Cellosolve acetate | 1.32 | 0.97 |
| 22A Methyl Cellosolve | 1.72 | 0.97 |
| 23 Diethyl ether | 0.23 | 0.72 |
| 23A Furan | | 0.94 |
| 24 Dioxane | 1.31 | 1.04 |
| 25 Methylal | 0.33 | 0.86 |
| 26 Diethyl sulfide | | 0.84 |
| 26A Carbon disulfide | 0.38 | 1.26 |
| 26B Dimethyl sulphoxide | 1.98 | 1.10 |
| 27 Propylene carbonate | 2.8 | 0.94 |
| 28 γ-Butyrolactone | 1.92 | 1.29 |
| 29 Acetone | 0.35 | 0.79 |
| 30 Methyl ethyl ketone | 0.42 | 0.81 |
| 31 Methyl isobutyl ketone | 0.59 | 0.80 |
| 31A Methyl isoamyl ketone | | 0.82 |
| 32 Diisobutyl ketone | 1.0 | 0.81 |
| 32A Isophorone | 2.6 | 0.92 |
| 32B Acetophenone | 1.9 | 1.03 |
| 33 Cyclohexanone | 2.2 | 0.94 |

Appendix A.3 (continued)

| | Viscosity Cp. | Specific gravity |
|---|---|---|
| 33A Tetrahydrofuran | 0.55 | 0.89 |
| 34 Mesityl oxide | 0.60 | 0.85 |
| 35 Ethyl acetate | 0.44 | 0.89 |
| 36 n-Butyl acetate | 0.74 | 0.87 |
| 36A Isoamyl acetate | | 0.88 |
| 37 Isobutyl isobutyrate | | 0.88 |
| 38 Acetonitrile | $0.38_{d}$ | 0.78 |
| 38A Butyronitrile | | 0.80 |
| 39 Nitromethane | $0.63_{b}$ | 1.13 |
| 40 Nitroethane | $0.77_{e}$ | 1.05 |
| 41 2-Nitropropane | 0.75 | 0.99 |
| 42 Aniline | 4.40 | 1.02 |
| 43 Nitrobenzene | $2.17_{d}$ | 1.20 |
| 44 Ethanolamine | 24.1 | 0.91 |
| 45 Dimethyl formamide | 0.80 | 0.95 |
| 46 Dipropyl amine | | 0.74 |
| 47 Diethyl amine | $0.37_{b}$ | 0.71 |
| 47A Morpholine | 2.37 | 1.00 |
| 47B Cyclohexylamine | | 0.86 |
| 47C Pyridine | 0.96 | 0.98 |
| 48 Carbon tetrachloride | 0.99 | 1.59 |
| 49 Chloroform | 0.37 | 1.48 |
| 50 Ethylene chloride | 0.84 | 1.26 |
| 51 Methylene chloride | 0.43 | 1.33 |
| 52 1,1,1 Trichloroethane | | 1.33 |
| 52A 1-Chlorobutane | 0.45 | .089 |
| 53 Trichloroethylene | 0.58 | 1.47 |
| 53A 2,2 Dichloro diethyl ether | 2.95 | 1.22 |
| 54 Chlorobenzene | 0.80 | 1.11 |
| 55 o-Dichlorobenzene | $1.27_{b}$ | 1.31 |
| 56 α-Bromonaphthaline | | 1.49 |
| 56A Cyclohexylchloride | | 1.02 |
| 57 Benzene | 0.65 | 0.88 |
| 58 Toluene | 0.59 | 0.87 |
| 59A Xylene | 0.67 | 0.87 |
| 59 Ethyl benzene | 0.42 | 0.87 |
| 60 Styrene | | 0.90 |
| 61 Tetralin | $2.00_{b}$ | 0.97 |
| 62 Hexane | $0.29_{b}$ | 0.69 |
| 63 Cyclohexane | 1.06 | 0.78 |
| 64 Water | 1.00 | 1.00 |
| 65 Acetic acid | 1.22 | 1.05 |
| 66 Formic acid | 1.78 | 1.22 |
| 67A Butyric acid | 1.54 | 0.96 |
| 68 Benzaldehyde | 1.52 | 1.05 |
| 69 Acetic anhydride | 0.91 | 1.08 |

$_{a}$-23°, $_{b}$-25°, $_{c}$-39°, $_{d}$-15°, $_{e}$-19°

# Summary

*Chapter 1*

The general scope and results of the study are discussed in perspective. Interactions among materials can be predicted from the solubility parameter. Solvent retention is controlled by solvent diffusion coefficients i.e. by solvent molecular structure and not by hydrogen or polar bonding.

*Chapter 2*

The development of the three dimensional solubility parameter is described. The initial trial and error approach to dividing the solubility parameter into components representing dispersion, polar, and hydrogen bonding contributions has been supplemented by independent calculation of the components. Approximately 10,000 observations have been explained by this concept. The system is based on polymer solubility and can explain such phenomena as the dissolving of a polymer in mixtures of non-solvents with exceptional accuracy.

*Chapter 3*

The characterization of materials with the three dimensional solubility parameter has been extended to non-ionic emulsifiers, dyes, and pigments. These materials, like polymers, are characterized by volumes of interaction in the system. This can be done since they interact most strongly with solvents having point locations within a given volume of the three dimensional system. Non-interacting solvents can be predictably mixed with other non-interacting solvents to yield an interacting solvent mixture for these materials also. Pigment charge phenomena are discussed.

*Chapter 4*

Practical aspects of the three dimensional solubility parameter are discussed. Materials having similar solubility parameters interact more easily with each other since they are of a similar nature. This simple generalization has been used to describe polymer solubility, the mutual solubility and compatibility of polymers and resins, and simple solvent-polymer-pigment interactions.

*Chapter 5*

The process of solvent evaporation is described as consisting of two phases. The first of these is controlled by boundary layer resistance to solvent loss, while the second is controlled by internal diffusion resistance to solvent loss. Solvent is retained in "dry" polymer films because it can not easily find a place to move to within the dense matrix of polymer chain segments surrounding it. Various factors affecting solvent retention are discussed,as well as the effect of retained solvent. Means to reduce or to predict solvent retention are given.

*Chapter 6*

The diffusion coefficients of solvents in polymers vary with concentration. Solutions to the diffusion equation for an exponentially varying diffusion coefficient have been evaluated enabling rapid interpretation of absorption and desorption data for this concentration dependence. The diffusion coefficients for methanol, ethylene glycol monomethyl ether, chlorobenzene, and cyclohexanone in poly-(vinyl acetate) at 25° C are given to demonstrate this type diffusion. Solvents with low diffusion coefficients are those which are retained longest in polymer films. The most sterically complex solvents have the lowest diffusion coefficients.

*Chapter 7*

Diffusion coefficients for chloro-36-benzene in poly(vinyl acetate) have been measured by an isotope technique in solutions containing 0.76 and 0.59 volume fraction solvent. This enables estimation of the diffusion coefficients for the entire concentration range for this system. These diffusion coefficients have been coupled with a boundary layer resistance to solvent evaporation to enable mathematical solution of the entire drying problem. Estimated solvent concentration gradients are given for various stages in the drying process.

*Chapter 8*

This chapter discusses some of the notions the author has had regarding application of the principles developed in his study. Included are comments on the design of new materials, means of characterizing materials, some aspects of solution thermodynamics, and the use of the solubility parameter to correlate surface phenomena.

# Resume

*Kapitel 1*

Studiets generelle formål og resultater diskuteres i et videre perspektiv. Vekselvirkninger mellem stoffer kan forudsiges ud fra deres opløselighedsparametre. Opløsningsmiddelretentionen kontrolleres af opløsningsmidlernes diffusionskoefficienter, d.v.s. af deres molekulære struktur og ikke af hydrogenbindinger eller polære bindinger.

*Kapitel 2*

Udviklingen af den tredimensionale opløselighedsparameter beskrives. Den oprindelige opdeling ved forsøg af opløselighedsparametren i bidrag stammende fra dispersionsbindinger, polære bindinger og hydrogenbindinger er suppleret ved uafhængige beregninger af komponenterne. Henved 10.000 observationer forklares på grundlag af dette begreb. Systemet er baseret på polymeres opløselighed og kan fuldt ud forklare sådanne fænomener som opløselighed af en polymer i blandinger af ikke-opløselighedsmidler.

*Kapitel 3*

Karakteriseringen af stoffer udvides til også at omfatte ikke-ionogene emulgatorer, pigmenter og opløselige farvestoffer. Disse stoffer karakteriseres på samme måde som polymere ved vekselvirkningsområder i systemet. Dette kan gøres, fordi stofferne vekselvirker stærkest med opløsningsmidler, der er placerede som punkter inden for et givet volumen i det tredimensionale system. Ikke-vekselvirkende opløsningsmidler kan forudsiges ved blanding med andre ligeledes ikke-vekselvirkende opløsningsmidler at give en vekselvirkende blanding også for disse stoffer. Pigmentladningsfænomener diskuteres.

*Kapitel 4*

Praktiske anvendelsesområder for den tredimensionale opløselighedsparameter diskuteres. Stoffer med ensartede opløselighedsparametre vekselvirker lettere med hinanden, fordi de er af samme natur. Denne enkle generalisation kan anvendes til at beskrive polymeres opløselighed, fælles opløselighed og forenelighed af polymere og harpikser samt enkle opløsningsmiddel-polymer-pigment vekselvirkninger.

*Kapitel 5*

Fordampningsprocessen for opløsningsmidler beskrives som bestående af to faser. I den første fase kontrolleres opløsningsmiddeltabet af modstanden i grænselaget, mens det i den anden fase kontrolleres af modstanden mod indre diffusion. Opløsningsmiddel tilbageholdes i »tørre« polymerfilm, fordi det har vanskeligt ved at finde plads at bevæge sig på i den tætte matrix af polymerkædesegmenter, der omgiver det. Fremgangsmåder til at reducere opløsningsmiddelretentionen gives.

*Kapitel 6*

Opløsningsmidlers diffusionskoefficienter i polymere varierer med koncentrationen. Løsninger til diffusionsligningen for en eksponentielt varierende diffusionskoefficient er blevet udviklet. Herved bliver det muligt hurtigt at behandle absorptions- og desorptionsdata for denne type koncentrationsafhængighed med god nøjagtighed.

Diffusionskoefficienterne for methanol, ethylenglycolmonomethylether, chlorbenzen og cyclohexanon i polyvinylacetat ved 25° C gives for at demonstrere denne type diffusion. Opløsningsmidler med lav diffusionskoefficient tilbageholdes længst i polymerfilm. De sterisk mest komplekse opløsningsmidler har de laveste diffusionskoefficienter.

*Kapitel 7*

Diffusionskoefficienten for chlor$_{36}$benzen i polyvinylacetat er bestemt ved hjælp af isotopteknik for opløsninger indeholdende 0.76 og 0.59 volumendele opløsningsmiddel. Dette tillader bestemmelsen af diffusionskoefficienter for hele koncentrationsområdet for dette system. Disse diffusionskoefficienter er kædet sammen med modstanden mod fordampning i grænselaget, således at hele tørringsforløbet kan beskrives ad matematisk vej.

*Kapitel 8*

I dette kapitel diskuteres nogle af de tanker, forfatteren har gjort sig vedrørende anvendelsen af de principper, der er udviklet under dette studium. Kommentarerne omfatter udvikling af nye stoffer, karakterisering af stoffer, nogle synspunkter vedrørende opløsningsprocessens termodynamik samt anvendelse af opløselighedsparametren ved korrelation af overfladefænomener.

# Literature Cited

Bird, R. B., W. E. Stewart and E. N. Lightfoot, "Transport Phenomena", John Wiley and Sons, New York, 1960.

Björkman, A., Svensk Papperstidn., **59,** No. 13, 477 (1956).

Blanks, R. F. and J. M. Prausnitz, Ind. and Eng. Chem. Fundamentals, **3,** No. 1, 1 (1964).

Böttcher, C. J. F., "Theory of Electric Polarization", Elsevier, New York, 1952, Chap. 3.

Brintzinger, H., R. Haug and G. Sachs, Farbe u. Lack, **58,** 5–10, 143–50, 522 (1952) and **60,** 15–24, 59–68, 95–103 (1954).

Brønsted, J. N., Compt. Rend. Lab. Carlsberg, Sér. Chim., **22,** 99 (1938).

Brønsted, J. N. and K. Volquartz, Trans. Farad. Soc., **35,** 576 (1939), and Trans. Farad. Soc. **36,** 619 (1940).

Brønsted, J. N., and J. Koefoed, Dan. Mat. Fys. Medd., **22,** No. 17, (1946).

Burrell, H., Official Digest, **27,** No. 369, 726 (1955).

Burrell, H., Official Digest, **29,** No. 394, 1159 (1957).

Burrell, H., VI F.A.T.I.P.E.C. Congress Book, 21 (1962).

Crank, J. –A– "The Mathematics of Diffusion", Oxford University Press, Oxford, 1956, pp. 241–48.

Crank, J. –B– ibid. p.p. 186–191, 207–210.

Crank, J. –C– ibid. p. 326.

Crowley, J. D., G. S. Teague and J. W. Lowe, J. Paint Technology, **38,** No. 496, 296 (1966); **39,** No. 504, 19 (1967).

Dimarzio, E. A. and J. H. Gibbs, J. Polymer Sci., Part A, **1,** 1417 (1963).

Doolittle, A. K., "The Technology of Solvents and Plasticizers", John Wiley and Sons, New York, 1954, p. 380.

Dyck, M. and P. Hoyer, Farbe und Lack, **70,** 522 (1964).

Flory, P. J., "Principles of Polymer Chemistry", Cornell Univ. Press., Ithaca, 1953.

Fowkes, F. M., in "Chemistry and Physics of Interfaces", Amer. Chem. Soc., Washington, 1965, p. 1.

Gardon, J. L., J. Phys. Chem., **67,** 1935 (1963).

Gardon, J. L., J. Paint Technology, **38,** No. 492, 43 (1966).

Goates, J. R., R. J. Sullivan and J. B. Ott, J. Phys. Chem., **63,** 589 (1959).

Hamann, K. and G. Florus, Farbe u. Lack, **62,** 260–67, 323–31 (1956).

Hays, D. R., Official Digest, **36,** No. 473, 605 (1964).

Hildebrand, J. and R. Scott, "The Solubility of Non-electrolytes", 3rd edition, Reinhold Publishing Corp., New York, 1949.

Hildebrand, J. and R. Scott, "Regular Solutions", Prentice-Hall Inc., Englewood Cliffs, N. J., 1962.

Jackson, W. J. Jr. and J. R. Caldwell, Advances in Chem. Ser. **48,** 185 (1965).

Jackson, W. J. Jr. and J. R. Caldwell, Papers Presented at The New York City Meeting, Sept. 1966, Organic Coatings and Plastics Chemistry, **26,** p. 160, p. 170.

Jenckel, E. and R. Huesch, Kolloid-Z., **130,** 89 (1953).

Johnson, P. A. and A. L. Babb, Chem. Revs., **56,** 387 (1956).

Jülke, E. K., "Über die Verdunstung von Lösungsmitteln aus Lackschichten", Promotionsarbeit, Eidgenössische Technische Hochschule in Zürich, 1962, p. 87.

Kishimoto, A. and K. Matsumoto, J. Polymer Sci., Part A, **2,** 679 (1964).

Koefoed, J., Faraday Soc. Discussion, No. 15, 207 (1953).
Kokes, R. J. and F. A. Long, J. Am. Chem. Soc., **75**, 6142 (1953).
Landolt-Börnstein, Zahlenwerte und Funktionen.
Liebermann, E. P., Official Digest, **34**, No. 444, 30 (1962).
Lindenfors, S., Das Papier, **21**, No. 2, 65 (1967).
Long, R. B., Ind. Eng. Chem. Fundamentals, **4**, 445 (1965).
Mellan, I., "The Behaviour of Plasticizers", Pergamon Press, New York, 1961.
Mellan, I., "Industrial Plasticizers", Pergamon Press, Oxford, 1963.
Moore, W. R. and R. Shuttleworth, J. Polymer Sci., Part A, **1**, 733 (1963).
Patton, T. C., J. Paint Techn., **38**, No. 498, 387 (1966).
Pascal, R. H. and F. L. Reig, Official Digest, **36**, No. 475, 839 (1964).
Petersen, A., Färg och Lack, **12**, No. 1, 4 (1966).
Pimentel, G. C. and A. L. McClellan, "The Hydrogen Bond", W. H. Freeman and Co., San Francisco, 1960, Chap. 7.
Prager, S. and F. A. Long, J. Am. Chem. Soc., **73**, 4072 (1951).
Schaeffer, W. D., American Ink Maker, **43**, No. 5, 54 (1965).
Sharpe, L. H. and M. Schonhorn, Advances in Chem. Ser., **43**, (1964), p. 189.
Sonnich Thomsen, E.–A– Farmaceuten, **29**, 44 (1966).
Sonnich Thomsen, E.–B– Dansk Kemi, **47**, 35 (1966).
Sørensen, P., J.O.C.C.A., **50**, No. 3, 226 (1967).
Vinther, A., Färg och Lack, **11**, No. 10, 317 (1965).
Walker, L. A., Science, **112**, 757 (1950).
Weast, R. C., Ed. "Handbook of Chemistry and Physics", 45th edition, The Chemical Rubber Co., Cleveland, 1964–5.
Weidner, G. L., Official Digest, **37**, No. 490, 1351 (1965).
Weisberg, H. E., Official Digest, **34**, No. 454, 1153 (1962).
Weiss, P., DECHEMA-Monographien, **51**, 99 (1964).
Zisman, W. A., Advances in Chem. Series, **43**, (1964), p. 1.