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HANDBOOK
of
SOLUBILITY
PARAMETERS
and
OTHER COHESION
PARAMETERS

Allan F. M. Barton

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CRC Handbook of Solubility Parameters and Other Cohesion Parameters

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CRC Press, Inc.
Boca Raton, Florida

Library of Congress Cataloging in Publication Data

Barton, Allan F. M.

Handbook of solubility parameters and other cohesion parameters.

Bibliography: p.

Includes index.

1. Solubility. 2. Cohesion. I. Title.

QD543.B22 1983 541.3'42 82-9653

ISBN 0-8493-3295-8

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Direct all inquiries to CRC Press, Inc., 2000 Corporate Blvd., N.W., Boca Raton, Florida, 33431.

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International Standard Book Number 0-8493-3295-8

Library of Congress Card Number 82-9653

Printed in the United States

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Professor Barton's scientific contributions have been made as the result of the application of a variety of physical and chemical techniques to pure and applied problems associated with the properties of liquids and solutions, rates of chemical processes and resource utilization. He has been involved with the Solubility Data Project of the International Union of Pure and Applied Chemistry since 1975, and is currently Chairman of the Liquid-liquid Subcommittee of the Commission on Solubility Data. His publications include the books *The Dynamic Liquid State* (1974) and *Resource Recovery and Recycling* (1979), as well as reviews and research papers on high pressure molten salt electrochemistry, liquid transport properties, kinetics of halate-halide reactions in aqueous solution, solid dissolution rates, and phase transitions.

In addition to liquid state properties, his present interests include the production of liquid fuels from biomass and the recovery of resources from wastes.

Dedicated to

my wife, June, for her present encouragement
my parents, for their past support
my daughters, Rowena and Charmian, for their future

ACKNOWLEDGMENTS

I wish to express my gratitude to

- the Radcliffe Science Library and Pergamon Press in Oxford, where I began this project during study leave from Murdoch University in 1979 while assisting with the Solubility Data Series of the International Union of Pure and Applied Chemistry
- the numerous academic and industrial scientists who responded generously to my requests for reprints and further details
- the library staff of Murdoch University who assisted patiently in my search for elusive information
- the Murdoch University graphics staff and the School of Mathematical and Physical Sciences secretarial staff, who participated willingly in the presentation of the cohesion parameter data
- my family, who never complained as the piles of papers increased and my patience decreased

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Chapter 1

INTRODUCTION

The use of solubility parameters and other cohesion parameters has one important aim: to provide a simple method of correlating and predicting the cohesive and adhesive properties of materials from a knowledge only of the properties of the components. There are numerous more sophisticated theories which can be employed if precise descriptions are required, but there are none which can be used more easily to estimate the properties of a mixture from those of its constituents.

A very useful analogy was made by Darby et al.³⁴³ when discussing the use of relative permittivities in the prediction of plasticizer-poly(vinyl chloride) behavior, and I am taking the liberty of modifying it. A *predictor* of mixing ability (solubility, compatibility, etc.) differs from a *measure* of mixing ability as a falling barometer differs from a rain gage: two components of a mixture do not need to be brought together before predictions can be made on their miscibility. The analogy can be taken further: neither the falling barometer as a predictor of rain nor the cohesion parameter as a predictor of mixing ability is completely adequate on its own, but each predictor is useful in its own right. A barometer is even more valuable when combined with additional meteorological information, and cohesion parameters are of greater value when considered along with other chemical data.

There have been numerous reviews on the subject of Hildebrand solubility parameters and other cohesion parameters, in many languages, and concentrating on various aspects. Some of these are listed in Table 1. In addition, many manufacturers of polymers, solvents, and other products are including cohesion parameters and interaction parameters in their specifications and are supplying information sheets on their use (Table 2), and cohesion parameters are being used in the texts of patents.^{502,1081,1297} Despite this increasing activity there has been no comprehensive overview of the diverse application of cohesion parameters, and it is clear that some groups of scientists and technologists are unaware of valuable developments made by other groups.

A major problem confronts anyone trying to bring all this information together, the tremendous range of application of cohesion parameters making a complete literature search extremely difficult. Although I have made every effort to be exhaustive in this respect, no doubt there are important contributions which I have inadvertently overlooked. As far as possible, publications up to mid-1980 have been included, with *Chemical Abstracts* and *Science Citation Index* searched to the end of 1980.

My intention here is to bring as much as possible of the published information on cohesion parameters together in one place, and to provide the bibliographic data necessary to make the remainder of the information available. At the same time I have introduced an SI unit, converted all numerical data into SI form with the conversion factors tabulated in Section 2.5, and developed a uniform terminology and notation. Although there will be resistance from some quarters to these changes, I believe that they are necessary, and that the sooner they are made, the better.

One of the methods of classifying the diverse applications of cohesion parameters, and one which I have found helpful in compiling this information, is based on the states of matter involved. A survey of publications on the subject shows that all combinations of interactions corresponding to the classification in Table 3 are represented. Solubility parameters were originally developed to explain liquid state properties, and it proved logical to deal in the first nine chapters primarily with interactions in the liquid state. This is followed by gases (Chapter 11), solids (Chapter 12), and polymers (Chapters 13 to 16). Surfaces and interfaces are introduced in Chapter 17, and this subject is extended to chromatography in the following chapter. The last chapter concentrates on biochemical systems. In this ar-

Table 1
**A SELECTION OF GENERAL REVIEWS ON COHESION PARAMETERS AND
 RELATED TOPICS**

Author	Topic	Language	Refs.
Ahmad, Yaseen	Group contributions	English	17,18,20
Ahmad, Yaseen	Polymers, group contributions	English	19,20
ASTM	Resins, polymers	English	79
Barton	General	English	112
Barton	Surfaces	English	112b
Bernardo and Burrell	General; plasticization	English	153
Blanks, Prausnitz	Solution thermodynamics	English	171,172,174
Burrell	U.S. applications	English	233
Burrell	General	English	235,238
Burrell	Polymers	English	234,237,239
Cammarata et al.	Biological	English	250
Cosaert	General	French, Flemish	308
Dack	Chemical reactivity	English	331-337
Fukunaga et al.	Phase transfer catalysis	Japanese	484
Gardon	General	English	496
Gardon, Teas	General	English	500
Geczy	General	Hungarian	507
Guzman	General	Spanish	577
Hadert	Polymer solvents	German	580
Hansen	General	English	595
Hansen	Coatings	English	597,598
Hansen, Beerbower	General	English	604
Imoto	General; adhesion	Japanese	699,700
Jayasri, Yaseen	Vaporization enthalpy	English	733
Johannsen	General	German	740
Kaelble	General, adhesion	English	747
Karger, Keller, et al.	Chromatography	English	770-772,779,780
Lucas	General	French	941
Mandik	General	Czech	965,969
Mandik, Kaspar	Film-forming polymers	Czech	971
Mandik, Korinsky	General	Czech	972
Mandik, Stanek	Coatings	Czech	974
Marti	General	German	988
Mellan	General	English	1021
Meyer zu Bexten	General	German	1030
Mitomo, Teshirogi	General	Japanese	1050
Moiseev, Pilyagin	Spraying solvents	Russian	1054
Moore	Fiber-forming polymers	English	1058
Nunn	General	English	1116
Rebenfeld et al.	Polymers	English	1225
Reichardt	General	English	1233-1235
Robu	General	Romanian	1267
Sandholm	Polymers	English	1312
Schoenmakers	Liquid chromatography	English, Dutch	1333a
Sevestre	General	English	1353
Sevestre	General	French	1354
Seymour	Polymers	English	1361-1363
Seymour	Polymers	Spanish	1364
Seymour, Sosa	General	English	1375
Shen	General	Chinese	1397
Shinoda	General	English, Japanese	1403
Skaarup	General	English	1428
Skelly	Textile processing	English	1429
Slepakova et al.	Polymer compatibility	Russian	1430

Table 1 (continued)
**A SELECTION OF GENERAL REVIEWS ON COHESION PARAMETERS AND
 RELATED TOPICS**

Author	Topic	Language	Refs.
Snyder	General	English	1441-1443
Sonnich Thomsen	General	Danish	1458-1459
Sonnich Thomsen	General	English	1460
Stawiszynski, Zawadzki	General	Polish	1489
Suzuki, Hagiwara	First transition systems	English	1516
Tager, Kolmakova	General	Russian	1520
Takada	General	Japanese	1521
Taylor	General	English	1542
Teas	Resins	English	1543-1545
Tlusta, Zelinger	General	Czech	1554
Watanabe	General	Japanese	1625, 1626
Weast	General	English	1632
Yoshida	General	Japanese	1698

Table 2
**A SELECTION OF MANUFACTURERS' BULLETINS AND
 PUBLICATIONS WHICH INCLUDE COHESION PARAMETER
 INFORMATION**

Company	Author	Refs.
Albert	Walz	1620, 1621
American Cyanamid	Nelson	1098
Ashland	Teas	1543-1545
BASF	Riedel	1256
Bendix	Jackson	722-729
Bostik	Harrison	613, 614
CIBA-Geigy	Skelly	1429
Commercial Solvents Corp.	Sausaman	1316
Dow Corning	Wessling	1639
	Yerrick, Beck	1697
Dunlop	Corish	306
du Pont	—	390, 391
	Cosaert	308
	Hagman	582
	Starkweather	1483
	Zunker	1715
Eastman	Crowley	322, 323, 394
Esso	Beerbower, Dickey	134
	Beerbower et al.	136
	Sheehan, Bisio	1392
Exxon	Funk	485
General Electric	Kambour	760-765
Hercules	—	642
	Orr	1133
Hoechst	Bohn	180-182
	Sattelmeyer	1314
Humble	Kirkland	801
ICI	Small	1433
	Vincent, Raha	1600
Imperial Smelting Corp.	Slinn	1431
Inmont	Burrell	235-241

Table 2 (continued)
A SELECTION OF MANUFACTURERS' BULLETINS AND
PUBLICATIONS WHICH INCLUDE COHESION PARAMETER
INFORMATION

Company	Author	Refs.
Isotron	—	715
Köge (KVK)	Sorensen	1447-1453
M & T Chemicals	Vinther	1602
	Gardon	498
Monsanto	Anagnostopoulos, Coran, Gamrath	53,55,305
	Darby, Touchette, Sears	343
	Wilt	1653
Neville Chemical Co.	—	1101
Pennsylvania Industrial Chemical Corp.	—	1180
Rohm & Haas	Brendley	203
	Gardon	496,497
Shell	—	1393-1396
	Nelson	1099,1100
	Nunn	1116
	Ramsbotham	1218-1220a
	Reynolds, Larson	1244
Technicon Instruments	Snyder	1440-1445
Union Carbide	—	1567
	Hoy	680,681
	Shaw	1391
Upjohn	Yalkowsky et al.	1684

Table 3
CLASSIFICATION OF COHESIVE AND
ADHESIVE INTERACTIONS INVOLVING
GASES (G), LIQUIDS (L), POLYMERS (P), AND
CRYSTALLINE SOLIDS (S)

Property	Interaction
Single phase, bulk	G, L, P, S
Interfacial	G-L, G-P, G-S, L-L, L-P, L-S, P-P, P-S
Dispersion	G-L, L-G, G-P, P-G, G-S, S-G, L-L, L-S, S-L, P-L, L-P, P-P, P-S, S-P, S-S
Miscibility	G-L, G-P, G-S, L-L, L-S, P-L, P-P, P-S
Phase change	G-L, L-G, L-S, S-L, P-S, S-P, G-S, S-G

rangement, each chapter draws on the concepts and data of previous chapters.

My general conclusions for all systems may be summarized as follows:

1. Hildebrand parameters (δ) provide a broad, qualitative indication of behavior for most systems, and good results for a very small number of hydrocarbons.
2. Hansen parameters (δ_d , δ_p , δ_h) and similar sets of partial cohesion parameters give an approximate quantitative measure of the extent of interactions for all systems and good results for a limited number of systems without significant specific chemical interactions.
3. A set of interaction cohesion parameters (δ_d , δ_o , δ_i , δ_a , δ_b) including separate Lewis acid and Lewis base terms, is necessary for a reliable quantitative evaluation of the

behavior of multicomponent systems. (This is not just because “more is better”, but because acid-base reactions are “unsymmetrical”, involving a donor and an acceptor with complementary roles.) It is also necessary to allow for differences in the molar volumes of the components, and there is scope for extension to ion-dipole and ion-induced dipole electrostatic cohesion parameters.

In a few areas (particularly chromatography) the subject has developed to stage (3); in others (e.g., polymer-solvent interactions such as paint formulation, and reverse osmosis membrane performance) it has reached stage (2); but in many others (notably biochemical and biocompatible systems) progress has not been made past Hildebrand parameters.

Chapter 2

THERMODYNAMICS

Molecular materials exist in the form of liquids and solids over certain ranges of temperature and pressure because in some circumstances the liquid and solid states are more stable than the corresponding gaseous state; that is, there are energetic advantages in having the molecules packed together in either random or ordered close-packed arrangements. In these condensed phases, strong attractive or cohesive forces exist between the molecules, and as a result each molecule is said to have a considerable negative potential energy relative to a vapor phase molecule which has negligible potential energy originating in this way. (Ionic liquids and crystals have even stronger attractive forces arising from coulombic interactions.)

2.1 COHESIVE ENERGY

If U is defined as the molar internal energy (the molar potential energy of a material relative to the ideal vapor at the same temperature) then U has a negative value. It follows, therefore, that the molar *cohesive energy* (the energy associated with the net attractive interactions of the material and defined as $-U$) has a positive value.

For a liquid, assuming that the intramolecular properties (those associated with individual molecules) are identical in gaseous and liquid states (which is true except in the case of complex molecules: see Table 19, Chapter 14) it can be seen that the molar cohesive energy can be divided into two parts:

1. The molar vaporization energy, $\Delta_1^g U$, required to vaporize a mole of the liquid to its saturated vapor
2. The energy $\Delta_1^z U$ required to expand the saturated vapor to infinite volume at constant temperature, that is, the energy necessary to completely separate the molecules

This can be expressed¹¹⁹⁹

$$-U = \Delta_1^g U + \Delta_1^z U = \Delta_1^g U + \int_{V=V_g}^{V=\infty} (\partial U / \partial V)_T dV \quad (1)$$

where V is the molar volume. The molar cohesive energy $-U$ can be subdivided further according to the relationship

$$-U = \Delta_1^g H + \Delta_1^z H - RT + p_s^l V \quad (2)$$

where

$\Delta_1^g H$ is the molar enthalpy of vaporization

$\Delta_1^z H$ is the increase in enthalpy on isothermally expanding one mole of saturated vapor to zero pressure

p_s is the saturation vapor pressure at temperature T

$^l V$ is the molar volume of the liquid (the superscript l frequently being omitted if there is no ambiguity)

R is the gas constant ($8.31441 \text{ J K}^{-1} \text{ mol}^{-1}$)