Structure–Solubility Relationships in Polymers

EDITED BY
FRANK W. HARRIS
RAYMOND B. SEYMOUR

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DEDICATION

It is a distinct and monumental occasion when a former president of the American Chemical Society serves as the keynote speaker for a symposium which is based on some of his original investigations. It certainly is in accord with this Centennial/Diamond Jubilee meeting when this 94 year old patriarch presents the principal talk at the president's dinner and the opening address of the symposium on the structure-solubility relationships in polymers.

His utilization of Occam's razor to reduce the complexity of solubility theories and his "From Then to Now" principal address are most appropriate for a Centennial meeting of a chemical society in which he has played a major role throughout his professional lifetime. We are confident that the authors of the following papers join with the chairmen in dedicating this book to Dr. Joel H. Hildebrand who is responsible for much of the progress that has been made in relating the solubility of polymers to their molecular structure.

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PREFACE

The papers contained in this book were presented in the symposium on "Structure-Solubility Relationships in Polymers" held by the American Chemical Society at its 172nd Meeting in San Francisco, August 30-September 3, 1976. The final manuscripts were collected at the meeting so that the authors could expand considerably on the brief abstracts that appeared in *Polymer Preprints* and could incorporate their most recent results. The joint sponsorship of this symposium by the Division of Polymer Chemistry and the Division of Organic Coatings and Plastics Chemistry in this centennial year for the Society was most appropriate. Polymer solutions have long been a major concern of the Coatings and Plastics Division due to their large consumption by the coatings industry, while theoretical and fundamental aspects of polymer solubility have appeared frequently in *Polymer Preprints*.

In organizing this symposium, we attempted to blend reports on the latest in solubility theory with experimental papers on the effects of structural modifications on solvent interactions. In fact, many of the contributed papers correlate modern solubility theory with experimental results. While seeking a nearly equal amount of industrial and academic participation, we also tried to cover a broad spectrum of polymer types. We feel that the result of these efforts is a comprehensive compilation of the recent significant work in polymer solubility.

We believe that the papers contained herein by the foremost authorities in the field are not only extremely informative but will also form the basis for considerable future research. Hence, we express our sincere appreciation to the contributors for making the symposium a great success and for making the publication of this volume possible.

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OPERATIONS ON SWOLLEN THEORIES WITH OCCAM'S RAZOR

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This is an opening address invited by chairman Drs. Seymour and Harris presumably in recognition of the author's contribution to solubility theories. This constitutes a critique of theories of liquids and transport phenomena that violate a principle stated by Alfred North Whitehead (Principle of Relativity, Cambridge University Press, 1922):

> The philosophy of science is the endeavor to formulate the most general characters of things observed. These sought-for characters are to be no fancy characters of a fairy tale enacted behind the scenes. They must be observed characters of things observed.

OPERATIONS ON SWOLLEN THEORIES WITH OCCAM'S RAZOR

Joel H. Hildebrand
University of California

William of Ockham, Surrey, England, born about 1300 A.D., became known as "the invincible doctor" because of his cutting criticism of ecclesiastical dogma. One of his utterances became famous as "Occam's Razor." In the original Latin it is:

Essentia non sunt multiplicanda praeter necessitatem

I translate it rather freely as: The theory of a phenomenon must not be more complicated than is necessary.

I employ this instrument to operate upon published explanations of phenomena in simple liquids. I know of no subject that has been too overloaded with complications.

My first illustration is the "cage model" of diffusion depicted in the book "The Solubility of Nonelectrolytes" by Hildebrand and Scott (1). A molecule is represented as imprisoned in a cage of molecules, bumping about with a certain frequency. Suddenly it acquires, from an unexplained source, an "activation energy" sufficient to enable it to burst out of its cage into a "hole" in a leap of one diameter. The unreality of that description of diffusion is explained in "Regular and Related Solutions" by Hildebrand, Prausnitz and Scott (2).

> Alder and Einwohner calculated mean free paths in dense fluids from a study of molecular dynamics of 10^6 free paths in a system of 500 hard spheres. . . . The fluid free path distributions. . . are without a peak near a particle diameter or . . . at any other distance. . . . At the highest density considered, $v/v_o = 1.6$, the probability of a free path longer than a hard sphere diameter is 4×10^{-8}.

In another paper, Alder and Hildebrand (3), in a brief communication wrote:

> The method most commonly used for representing the temperature dependence of viscosity and diffusivity of liquids is to plot their logarithms against $1/T$, by analogy with the Arrhenius equation for chemical rate constants, and interpreting the slopes of the

> lines thus obtained as "activation energy." This designation implies the presence of barriers against freedom of flow, imagined as consisting of some sort of quasi-lattice structure. We wish to call attention to evidence that no activation is involved in these processes, and that their variations with temperature are quite accurately represented by nonexponential equations. . . .
>
> All molecules participate equally in the thermal agitation that produces random disorder. . . . Vacancies that may exist in a crystal become randomly distributed in liquid as intermolecular space. . . . No directive force. . . acts upon molecules of a nonpolar liquid. They diffuse simply because thermal motions keep them ever on the move.

Evidence of maximum disorder can be seen in the entropy of vaporization of nonpolar liquids, illustrated in Fig. 1.

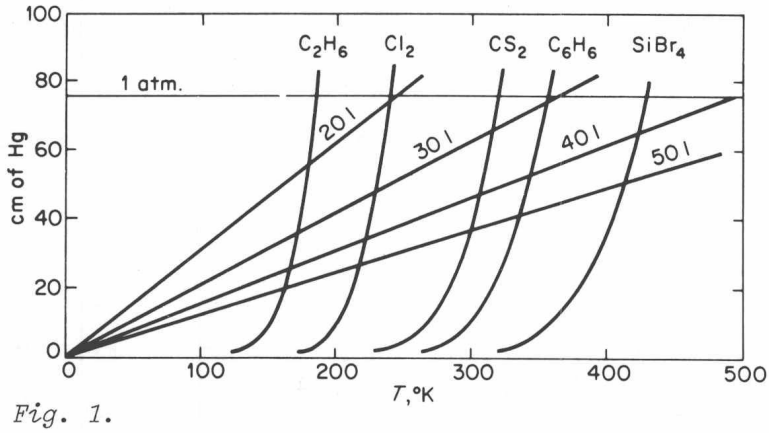

Fig. 1.

Vapor pressures below one atmosphere are plotted againt $\underline{T}$ for a number of liquids. The straight lines represent different volumes. The tangents at the intercepts multiplied by $\underline{R}$ give values of entropy of vaporization; they are equal to the same volume of vapor. It is a kind of "corresponding states" relation. It has been called "the Hildebrand rule." It replaces the "Trouten rule," which compares entropies at one atmosphere, where slopes are not the same. Associated liquids give steeper vapor pressure curves and larger values of entropy of vaporization; therefore agreement with the Hildebrand rule indicates maximum freedom of molecular motions in the liquid.

Hermsen and Prausnitz (4) calculated values of entropy of vaporization to 49.5 liters of 20 alkanes whose boiling points range from 92.6K to 611.9K. The values found were all 22.3 ± 0.1 cal. deg^{-1} mol^{-1}. This finding rules out all structured models, with their "cages," cells," clusters" and "liquid lattices." It permits statistical calculation of relative numbers of contacts of like and unlike species of molecules in a mixture. It indicates that simple liquids have no structure. Crystal structure completely vanishes upon melting; infinitessimal stress suffices to cause a liquid to flow.

The thermodynamic "equation of state" of simple liquids is:

$$\underline{P} + (\delta \underline{E}/\delta \underline{V})_{\underline{T}} = \underline{T}\,(\delta \underline{S}/\delta \underline{V})_{\underline{T}} = \underline{T}\,(\delta \underline{P}/\delta \underline{T})_{\underline{V}}$$

It is approximated by the van der Waals equation where $(\delta \underline{E}/\delta \underline{V})_{\underline{T}}$ is $a/\underline{V}^2$. The exponent 2 is approximately valid for the rare gases, but increases with molecular complexity as illustrated in Table 1.

TABLE 1

	$\underline{n}$ in $\delta \underline{E}/\delta \underline{V} = \underline{V}^{\underline{n}}$
CCl_4	2.09
$C_2Cl_3F_3$	2.19
$c\text{-}C_4Cl_2F_6$	2.35
$c\text{-}C_6F_{11}CF_3$	2.44

$\underline{P}$ increases linearly with $\underline{T}$ at constant volume over long ranges, hence $(\delta^2 \underline{P}/\delta \underline{T}^2)_{\underline{V}} = 0$ and $(\delta \underline{CV}/\delta \underline{V})_{\underline{T}} = 0$

In passing along a continuous van der Waals path from gas to liquid above the critical temperature, at no point does any sort of structure enter the fluid.

My next sample of complexity far in excess of necessity is an equation for calculating the viscosity of a simple liquid:

$$\eta = \frac{Nh}{V}\,\frac{1}{(1 - e^{-\vartheta/T})}\,\frac{6}{\eta k}\,\frac{V}{(V-V_3)}\,\exp\frac{a'E_3V_3}{(V-V_3)RT} + \frac{V - V_3}{V}\,\frac{(2mkT)^{1/2}}{3\Pi^{3/2}d^2}$$

I give no reference because this is a critique of procedures, not persons.

My chief purpose in research has been to understand natural phenomena. Max Born well described it when he wrote:

> The problem of physics is how the actual phenomena, as observed with the help of our sense organs aided by instruments, can be reduced to simple notions which are suited for precise measurement and used for the formulation of quantitative laws.

As I contemplated "actual" data for the viscosity of a simple liquid such as propane as it changes with temperature, the "simple notion" occurred to me that the flow of a liquid produced by applying vector momentum should be proportional to the free space between the molecules. Expressed in the shorthand of algebra this is

$$\Phi = \underline{B}\ (\underline{V} - \underline{V}_o)/\underline{V}_o = 1/\eta$$

This remains linear for simple liquids to high pressures (544 atmospheres for propane, and up to molar volumes well above boiling point volumes.) Divergence begins as mean free paths become long enough for molecules to acquire random thermal momenta sufficient to oppose the applied vector momentum (Fig. 2).

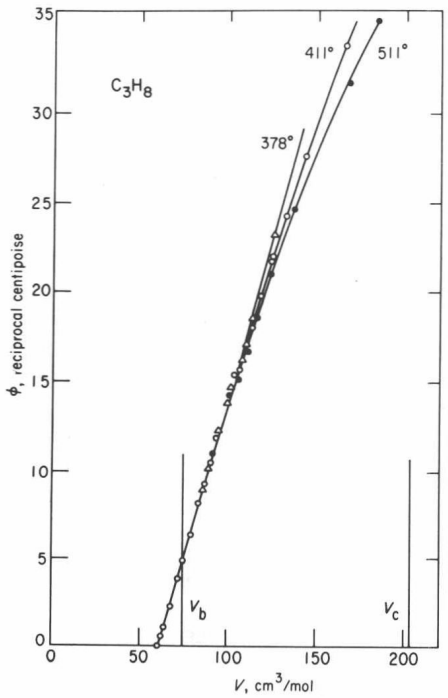

Fig. 2.

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