An improvement in the theory of regular solutions
(solubility parameters/methyl groups/iodine solubility/London forces)

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ABSTRACT In constructing the theory of regular, nonpolar, binary solutions, the partial molal energy of mixing has been expressed by the square of difference between "solubility parameters," usually evaluated by the molal energy of vaporization per cubic centimeter, \((\Delta E^{\prime}/V)^{1/2} = \delta\), at approximately 25°C. We have found, however, that liquids whose molecules contain methyl groups do not conform to these parameters; to account for their solvent power for iodine requires parameters increased in proportion to the number of methyl groups per molecule. The anomaly may be attributed to the absence of outer nonbonded electrons able to exert London attractive force between neighboring molecules. Parameters derived from solubility for iodine in both methyl-containing liquids and fluorochemicals greatly improve the predictive power of the theory of regular solutions.

The theory of solubility of nonelectrolytes set forth in the book Regular and Related Solutions, by Hildebrand, Prausnitz, and Scott (1), is based upon two concepts: (i) that the components are randomly mixed by thermal agitation, to give the entropy of solution, and (ii) that the energy of mixing can be calculated by solubility parameters, \(\delta\), that are square root of the energy of vaporization per cubic centimeter of the liquid, \((\Delta E^{\prime}/V)^{1/2} = \delta\). The basic equation is, for component 2,

\[RT \ln a_2/x_2 = V_2 \phi_2 \delta_2^2 - V \phi_1 \delta_1^2, \tag{1}\]

in which \(a\) is activity referred to the pure liquid, \(x_2\) is mole fraction, \(V_2\) is molal liquid volume, \(\phi_1\) is the molal volume fraction of the other component. Fig. 1 (from page 148 of ref. 1) is a plot of the solubility of iodine in different groups of solvents at 25°C. The activity of solid iodine at this temperature is 0.258, its under-cooled liquid volume is 59 cm³, and \(\delta_2 = 14.1\). Reverse subscripts for component 1.

The points on line A are for the solubility of iodine at 25°C in CS₂, CHCl₃, TiCl₄, cis-decalin, trans-decalin, CCl₄, cyclo-C₄H₈, cyclo-C₆H₁₀, SiCl₄, and CCl₃CF₃. The three points off the line at the top are for solutions in (C₂F₅)₂N, C₇F₁₆, and cyclo-C₂F₅CF₃. The three points G are for polar liquids, those on line F are for aromatics that form brown complexes with iodine; neither of these groups obeys Eq. 1, nor should they. They are treated as deviants from line A. But the points BCDE, all alkanes, and the lone point to the right, for octamethylcyclopentasiloxane, cyclo-(SiO)₄(CH₃)₆, all form violet solutions. The requires explanation.

In 1950 I published a paper (2) on "An irregularity in the solvent powers of paraffins." In the same year, Fisher, Benesi, and I (3) published five liquid–liquid solubility curves with perfluorohexane and stated in a summary that, "Solubility parameter differences calculated from the experimental results were in close agreement with values predicted by solubility theory for all but the two paraffins, n-C₇H₁₅ and 2,2,4-trimethylpentane."

Scott (4) in 1958 published "The anomalous behavior of fluorocarbon solutions."

In ref. 1, p. 98 and following, we wrote, "Regular solution theory is useful for semiquantitative work; for quantitative results it is necessary to make empirical modifications. While such modifications can be made in several ways, the most direct way is to introduce corrections to the geometric mean." This is involved in \((\delta_1 - \delta_2)^2 = \delta_1^2 + 2\delta_1 \delta_2 + \delta_2^2\). We discussed this at some length. This hypothesis was unsatisfactory because it was not predictive; it had no theoretical basis. Dymond and I (5) in 1965 published "Effect of methyl groups upon solvent power of aliphatic liquids." For this there is a theoretical explanation, which I pointed out in 1978 (6) under the title "Absence of outer nonbonding electrons in methyl groups affects solubility parameters." London (7), in 1950, explained the van der Waals attraction between nonpolar molecules as a quantum theory perturbation between electrons in outer orbitals of neighboring molecules. The electrons in methane and methyl groups are all in tight bonds; the ionization potential of methane, 13.0 eV, is extraordinarily large, and the intermolecular attractions are so small that \(\Delta E^{\prime}/V\) is too small to measure their attraction with molecules like those of iodine.

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FIG. 1. Solubility of iodine in different groups of solvents, described in the text. Coordinates are the members of Eq. 1. (One kilocalorie = 4.184 kilojoules.) (Originally printed in ref. 5).
I show in Table 1 the values of the parameters that these methyl compounds must have in order to account for their solvent power for iodine. The increase is proportional to the number of methyl groups in molecules of the solvent as shown in Fig. 2. Shinoda and I (8) calculated, similarly, the solubility parameters of the fluorochemicals that place on the line the three points near the top of line A in Fig. 1 and are included in Table 1.

The question next arises, will these new parameters serve to predict solubility relationships of these liquids with other substances? The first test is the solubility of SnI4 in isooctane measured in 1937 by Negishi (9), who obtained x2 = 0.0032. With the old parameter for isooctane the calculated value of x2 = 0.000215; the new parameter yields 0.0028.

Next, I use liquid—liquid solubilities for C7F16CF3 with cyclo(SO)3(CH3)4 with its eight methyl groups, determined by Joly and Hildebrand (10) in 1957. Its critical mixing temperature is 44°C and there are enough solubility points on the A and B branches to yield A and B values of x for each component at 40°C. This makes it possible to calculate a value of (δ2 - δ1)2 more reliable than a value calculated from the critical temperature, as has been the custom. We use formula 10.3 from page 174 of ref. 1. x1A = 0.84, x1B = 0.39, x2B = 0.61, x2A =

![Graph](http://example.com/graph.png)

**Fig. 2.** Increases in solubility parameters of solvents for iodine in relation to the number of methyl groups in a molecule.

Table 2. Parameters of isooctane/(C4F9)3N mixture

<table>
<thead>
<tr>
<th>Phase</th>
<th>x_A</th>
<th>x_B</th>
<th>φ_A</th>
<th>φ_B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isooctane</td>
<td>0.277</td>
<td>0.9663</td>
<td>0.1038</td>
<td>0.8771</td>
</tr>
<tr>
<td>(C4F9)3N</td>
<td>0.723</td>
<td>0.0335</td>
<td>0.8962</td>
<td>0.1029</td>
</tr>
</tbody>
</table>

0.16, V1 = 196, V2 = 312, from which we obtain δ2 - δ1 = 2.36. The old values are δ1 = 6.4 and δ2 = 6.1, which are quite inconsistent with the limited solubility, but the iodine-based parameters give 8.2 - 5.6 = 2.6, in reasonable agreement with 2.36.

The curve for C7F16 and isooctane obtained by Fisher and Benesi (3), critical temperature = 23.7°C, permits calculating at 20°C to give δ2 - δ1 = 2.52; the revised parameters give 7.9 - 5.6 = 2.3.

Another test of a parameter based upon solvent power for iodine is the formula for the partial molar volume of a solute liquid at high dilution. On p. 186 of ref. 1 there are 19 liquid pairs in which the excess of the partial molar volume of the dilute solute over its pure molar volume V° agrees with the relationship:

\[
\frac{\bar{V}_2 - V^0_2}{V^0_2} = \left(\frac{\delta_2 - \delta_1}{\partial (E)/\partial V}\right) \tau
\]

in which \(\tau\) indicates Kelvin temperature. The measured expansions of isooctane in CS2 and in CC14, 0.037 and 0.009, respectively, are not calculated correctly by using the value \((\Delta E/V)/V_0 = 6.8\), but by using its iodine-based parameter 7.9 gives 0.049 with CS2 and 0.006 with CC14. [The value of \((\partial E/\partial V)\) is 89.0 for CS2 and 81.0 for CC14.]

The evidence seems to show that the solubility parameters derived from solvent power for iodine can predict with reasonable accuracy the solubility relationships of the solvents with each other.

Although the London concept of the mechanism of the attractive forces between nonpolar molecules is not yet quantitative, the solubility parameters of regular solution theory adjusted to solvent power for iodine yield predictions that are good approximations.