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Prediction of Hansen Solubility Parameters with a New Group-Contribution Method

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Abstract A group-contribution method for the estimation of Hansen solubility parameters of pure organic compounds is presented. It uses two kinds of characteristic groups: first-order groups that describe the basic molecular structure of compounds and second-order groups, which are based on the conjugation theory and improve the accuracy of predictions. A large variety of characteristic groups ensure the prediction of Hansen solubility parameters for a broad series of organic compounds, including those having complex multi-ring, heterocyclic, and aromatic structures. The predictions are exclusively based on the molecular structure of compounds, and no experimental data are needed. The predicted values permit a fairly reliable selection of solvents based on the radius of a Hansen solubility parameter sphere or on a Teas parameter ternary plot. Especially designed algorithms permit the preparation of a list of new molecular structures which, if synthesized, could be the ideally suited solvents for a series of corresponding applications.

Keywords Group-contribution method · Hansen solubility parameters

1 Introduction

The *solubility parameter* is an important concept that can be used, among other applications, for the rational selection of solvents. Both the total solubility parameter [1] and its constituent partial solubility parameters (Hansen solubility parameters) [2] are widely used for the selection of appropriate solvents for given solutes. The use of the solubility parameter for the selection of solvents is based on the well-known rule of chemistry: "like dissolves like" [3]. Thus, if the intermolecular forces between

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the molecules of the solvent and between the molecules of a solute are of a similar strength, the solvent is usually a *good solvent* for this solute.

The Hildebrand total solubility parameter [1], δ_t, is defined as the square root of the cohesive energy density:

$$\delta_\mathrm{t} = \sqrt{\frac{E_\mathrm{coh}}{V}} \tag{1}$$

The cohesive energy is given by

$$E_\mathrm{coh} = \Delta H_{v,298} - RT \tag{2}$$

where $\Delta H_{v,298}$ is the standard enthalpy of vaporization at 298 K, R is the universal gas constant, and T is the absolute temperature.

Thus, at any temperature T we may write

$$\delta_\mathrm{t} = \sqrt{\frac{\Delta H_v - RT}{V}} \tag{3}$$

where V is the molar volume at temperature T.

For polar compounds, as well as for compounds that contain hydrogen bonds, the total solubility parameter is, as a rule, not sufficient to describe their solubility behavior. This occurs because, in these compounds and in general terms, three kinds of intermolecular forces can be present: dispersion, polar, and hydrogen-bonding forces. Dispersion forces are omnipresent intermolecular forces of low strength and are the only forces that hold non-polar symmetrical molecules together, for example, the molecules of ethane. Non-symmetrical molecules, those having a dipole moment, interact with polar forces of varying strength. Classic hydrogen-bonding forces occur in substances where hydrogen (proton)—donor and proton—acceptor groups are present. In the widely recognized hydrogen bonds, proton donors are groups where hydrogen atoms are directly attached to oxygen or nitrogen or fluorine atoms.

A significant enhancement of the predictive capacity and usefulness of the solubility parameter has been developed by the introduction of Hansen or partial solubility parameters [2]. Equation 4 describes the relation between the total solubility parameter, δ_t, and the Hansen solubility parameters, δ_d, δ_p, and δ_hb.

$$\delta_\mathrm{t} = \sqrt{\delta_\mathrm{d}^2 + \delta_\mathrm{p}^2 + \delta_\mathrm{hb}^2} \tag{4}$$

where δ_d is the dispersion Hansen solubility parameter, δ_p is the polar Hansen solubility parameter, δ_hb is the hydrogen-bonding Hansen solubility parameter.

The unit of solubility parameters is $(\mathrm{MPa})^{(1/2)}$ in the SI system of units.

The hydrogen-bonding Hansen solubility parameter includes not only classic hydrogen bonding but also other forms of electron exchange. Our group contributions in the present article correctly produce “hydrogen-bonding” values for molecules that would not be considered as classic hydrogen bonders.

The locations of common solvents can be depicted as points on δ_p versus δ_{hb} plots [4]. The "distances" (R_a) between materials 1 and 2 on such plots can be calculated using

$$R_a^2 = 4(\delta_{d1} - \delta_{d2})^2 + (\delta_{p1} - \delta_{p2})^2 + (\delta_{hb1} - \delta_{hb2})^2 \tag{5}$$

In this equation, the subscript "1" might refer to a polymer to be diluted, whereas the subscript "2" might refer to the challenge chemical or potential solvent.

In this respect, another interesting parameter is the *RED* number. The definition of the *RED* number is expressed as

$$RED = \frac{R_a}{R_o} \tag{6}$$

In this equation, R_o is the radius of a Hansen solubility parameter sphere and represents the largest value for R_a allowed where solubility (or other interaction being correlated) is allowed [4]. Good solvents have a *RED* number less than 1.0. Progressively poorer solvents have increasingly higher *RED* numbers.

Hansen solubility parameters can also be used in the equivalent form of Teas parameters [5]. With these parameters, each compound is represented by a single point in a ternary plot. The total sum of Teas parameters is equal to 1, but they are usually expressed as a percentage, or

$$100 f_d = \frac{100\delta_d}{\delta_d + \delta_p + \delta_{hb}} \tag{7}$$

$$100 f_p = \frac{100\delta_p}{\delta_d + \delta_p + \delta_{hb}} \tag{8}$$

$$100 f_h = \frac{100\delta_{hb}}{\delta_d + \delta_p + \delta_{hb}} \tag{9}$$

where f_d is the dispersion component of the fractional cohesion or Teas parameter, f_p is the polar component, and f_h is the hydrogen-bonding component.

2 Prediction of Solubility Parameters

2.1 Existing Group-Contribution Methods for Estimation of Solubility Parameters

Hoftyzer and van Krevelen [6] established a method for estimating the partial solubility parameters of polymers and pure organic compounds from group contributions. Their equation for the estimation of δ_d is as follows [7]:

$$\delta_d = \frac{\sum F_{di}}{V} \tag{10}$$

where F_{di} are the group contributions of type i to the dispersion component, F_d, of the molar attraction constant.

The equation for the estimation of δ_p is the following:

$$\delta_\mathrm{p} = \frac{\sqrt{\sum F_{\mathrm{p}i}^2}}{V} \tag{11}$$

where $F_{\mathrm{p}i}$ are the group contributions to the polar component, F_p. When two identical polar groups are present in a symmetrical position, the δ_p value calculated by Eq. 11 must be multiplied by a symmetry factor of
0.5 for one plane of symmetry,
0.25 for two planes of symmetry, and 0 for more planes of symmetry.
The corresponding equation for the estimation of δ_hb is the following:

$$\delta_\mathrm{hb} = \sqrt{\frac{\sum E_{\mathrm{h}i}}{V}} \tag{12}$$

where $E_{\mathrm{h}i}$ is the hydrogen-bonding energy per structural group i. For molecules with several planes of symmetry, $\delta_\mathrm{hb} = 0$. The group contributions, $F_{\mathrm{d}i}$, $F_{\mathrm{p}i}$, and $E_{\mathrm{h}i}$, for 28 structural groups are given in Ref. [7].

Hoy [8,9] established a different group-contribution method to estimate the solubility parameters. In this method, a system of equations must be used. This system contains four additive molar functions, auxiliary equations, and the final expressions for the components of δ.

The additive molar functions which are used in Hoy's method, in the case of low-molar mass liquids (solvents), are the following:

$$F_\mathrm{t} = \Sigma \mathrm{N}_i F_{\mathrm{t},i} \tag{13}$$

$$F_\mathrm{p} = \Sigma \mathrm{N}_i F_{\mathrm{p},i} \tag{14}$$

$$V = \Sigma \mathrm{N}_i V_i \tag{15}$$

$$\Delta_T = \Sigma \mathrm{N}_i \Delta_{T,i} \tag{16}$$

In Eqs. 13–15, F_t is the molar attraction function, F_p is its polar component, and V is the molar volume. Δ_T in Eq. 16 is the Lydersen correction for non-ideality [10], which is used in the auxiliary equations. The auxiliary equations are the following:

$$\log\alpha = 3.39\left(\frac{T_\mathrm{b}}{T_\mathrm{cr}}\right) - 0.1585 - \log V \tag{17}$$

$$\left(\frac{T_\mathrm{b}}{T_\mathrm{cr}}\right) = 0.567 + \Delta_T - (\Delta_T)^2 \tag{18}$$

where α is the molecular aggregation number which describes the association of molecules, T_b is the boiling point, and T_cr is the critical temperature. Equation 18 is the Lydersen equation.

The expressions for δ components are the following:

$$\delta_{\mathrm{t}} = \frac{F_{\mathrm{t}} + B}{V}, \quad B = 277 \tag{19}$$

$$\delta_{\mathrm{p}} = \delta_{\mathrm{t}} \left(\frac{1}{\alpha} \frac{+F_{\mathrm{p}}}{F_{\mathrm{t}} + B} \right)^{1/2} \tag{20}$$

$$\delta_{\mathrm{hb}} = \delta_{\mathrm{t}} \left(\frac{\alpha - 1}{\alpha} \right)^{(1/2)} \tag{21}$$

$$\delta_{\mathrm{d}} = \left(\delta_{\mathrm{t}}^2 - \delta_{\mathrm{p}}^2 - \delta_{\mathrm{hb}}^2 \right)^{1/2} \tag{22}$$

In Eqs. 19 and 20, B is the base value.

2.2 Our Group-Contribution Method

The Hildebrand total solubility parameter, δ, at 25 °C is one of the properties predicted by our previous group-contribution method [11]. The method includes a large variety of first-order and second-order groups and is able to estimate properties of organic compounds with complex multi-ring, heterocyclic, and aromatic structures. These compounds are of significant importance for the chemical, biochemical, pharmaceutical, and food industries, as well as for environmental protection.

However, as already mentioned, the use of Hansen solubility parameters is much more appropriate than the total solubility parameter for the selection of solvents. In the present study, our previous group-contribution method is extended for the prediction of Hansen solubility parameters. It is clear that the development of such a predictive method is of crucial importance not only for selecting the appropriate solvents for each given solute but also for the synthesis of new solvents with desired solubility and other properties.

In our method, the molecular structure of each organic compound can be described using two kinds of functional groups: first-order groups (UNIFAC groups) that describe the basic molecular structure of compounds and second-order groups that are based on the conjugation theory. The second-order groups give a physical meaning to the method, and this is an advantage compared to other group-contribution methods. Second-order groups improve the accuracy of predictions significantly.

The definition of second-order groups is based on the ABC framework [12]. According to this framework, each compound is represented as a hybrid of many conjugate forms. Every conjugate form is considered as a structure with integer-order localized bonds and integer charges on atoms. The purely covalent conjugate form is the dominant conjugate, and the ionic forms are the recessive conjugates, which are generated by using a conjugate operator. When a conjugate operator is applied to a dominant conjugate, it can generate a series of recessive conjugates. Conjugate operators consist of subchains with two or three bonds, such as O=C–C or C–C–C–H.

In the ABC framework, the properties of each compound are estimated by combining the corresponding properties of its conjugate forms. The properties of the conjugate forms are estimated through conjugation operators. Each operator has a fixed contribution, which is determined through regression and reflects the contribution of a whole series of conjugate forms. The basic property in the ABC framework is the standard enthalpy of formation at 298 K. For the estimation of this property, the contributions of the conjugate forms can be expressed in terms of their physical significance rather than adjustable parameters. Therefore, the most important conjugate forms, i.e., the forms that exert the strongest influence on the standard enthalpy of formation (and also on the other properties to be estimated), can be distinguished. The conjugation operators that are related to the most important conjugate forms make the largest contributions. It is possible to identify the classes of conjugate forms with the highest conjugation activity by examining the contributions of their operators.

The determination of second-order groups is based on the following principles [13]:

(i) The structure of a second-order group should incorporate the distinct subchain of at least one important conjugation operator, e.g., the CH_3COCH_2 second-order group incorporates the O=C–C, the O=C–C–H, and C–C–C–H operators.
(ii) The structure of a second-order group should have adjacent first-order groups as building blocks and it should be as small as possible, e.g., the CH_3COCH_2 second-order group has the CH_3CO, and CH_2 first-order groups as building blocks.
(iii) Second-order groups based on common operator(s) should be equally treated in the method. For example, $CH_n{=}CH_m{-}CH_p{=}CH_k\{n,k,p,m \in (0,2)\}$ represent the second-order groups obtained by the C=C–C=C operator.
(iv) The performance of second-order groups is independent of the molecule in which the groups occur. This is a fundamental group-contribution principle.

The methodology that is followed for the identification of second-order groups is as follows [11]:

(a) Identification of all first-order groups present in the structural formula of a given compound.
(b) Definition of all possible substructures of two or three adjacent first-order groups.
(c) Identification of all two-bond and three-bond conjugation operators in the substructures.
(d) Estimation of the conjugation operator energy of all substructures by addition of the energies of all of the conjugation operators.
(e) Identification of substructures with much higher conjugation energies than the others. These substructures are the second-order groups.

In our method, the basic equation that gives the value of each property from the molecular structure is:

$$f(x) = \sum_i N_i C_i + W \sum_j M_j D_j \tag{23}$$

where C_i is the contribution of the first-order group of type i that appears N_i times in the compound and D_j is the contribution of the second-order group of type j that appears M_j times in the compound. $f(x)$ is a single equation of the property, x, and is selected after a thorough study of the physicochemical and thermodynamic behavior of the property. The constant W is equal to 0 for compounds without second-order groups and equal to 1 for compounds which have second-order groups. Tables with first-order and second-order groups are reported below, and thus, the use of Eq. 23 is quite straightforward.

The determination of group contributions is done by a two-step regression analysis. In the first step of the regression, the aim is to determine the first-order group contributions only (that is, the C_i's). In the second step, using the C_i's contributions, the second-order groups are activated and the second-order group contributions (D_j's) are calculated through regression. These contributions act as a correction to the first-order approximation.

The Levenberg–Marquardt approach was used to minimize the total sum of squared errors between the experimental and predicted values of properties. This was the criterion for the selection of the most appropriate equation to fit the experimental data. The model is applicable to organic compounds with three or more carbon atoms, excluding the atom of the characteristic group (e.g., –COOH or –CHO).

2.3 Estimation of Hansen Solubility Parameters

By applying our group-contribution method for the estimation of Hansen solubility parameters, it was concluded that the linear version of the mathematical model fit the experimental data best. The equations for the estimation of Hansen solubility parameters are the following:

$$\delta_{\mathrm{d}} = \left(\sum_i N_i C_i + W \sum_j M_j D_j + 17.3231\right) \mathrm{MPa}^{(1/2)} \tag{24}$$

$$\delta_{\mathrm{p}} = \left(\sum_i N_i C_i + W \sum_j M_j D_j + 7.3548\right) \mathrm{MPa}^{(1/2)} \tag{25}$$

$$\delta_{\mathrm{hb}} = \left(\sum_i N_i C_i + W \sum_j M_j D_j + 7.9793\right) \mathrm{MPa}^{(1/2)} \tag{26}$$

It should be stressed that Eqs. 25 and 26 are valid only for Hansen solubility parameter values greater than 3 $\mathrm{MPa}^{(1/2)}$. The statistical values of the first-order and second-order approximations for the prediction of Hansen solubility parameters are presented in Tables 1 and 2. Figures 1–3 show the correlation between estimated and experimental values of Hansen solubility parameters.

Contributions of first-order groups to Hansen solubility parameters are shown in Table 3. For many compounds, first-order groups are sufficient. Estimations for some compounds, as already mentioned, can be improved with the introduction of second-order groups. Second-order group contributions are presented in Table 4. The group contributions to δ_{d} have also been included in the 2nd edition of Hansen's handbook

Table 1 Comparison of total sum of squared errors for first- and second-order approximations

Total sum of squared errors	First-order approximation	Second-order approximation	Change (%)
δ_d	128	116	−9.4
δ_p	713	465	−34.8
δ_{hb}	514	438	−14.8

Table 2 Average absolute error (AAE)[a] for first- and second-order approximations

	First-order approximation AAE (MPa$^{(1/2)}$)	Second-order approximation AAE (MPa$^{(1/2)}$)	Change (%)
δ_d	0.44	0.41	−6.8
δ_p	1.05	0.86	−18.1
δ_{hb}	0.88	0.80	−9.1

[a] Average Absolute Error = AAE = $\frac{1}{N}\sum\left|X_{est} - X_{exp}\right|$ where N is the number of data points, X_{est} is the estimated value of solubility parameters, and X_{exp} is the experimental value

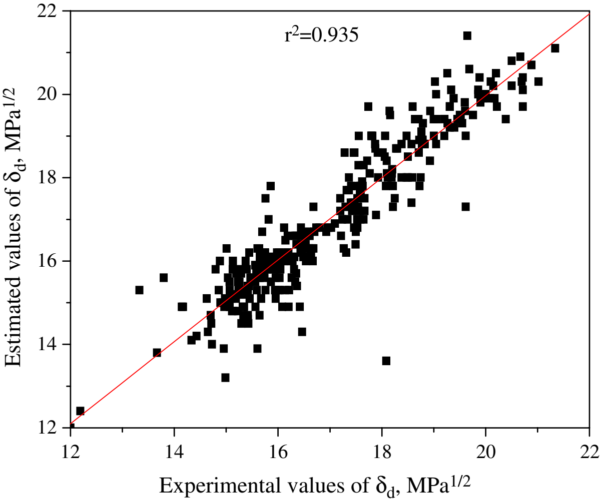

Fig. 1 Correlation between estimated and experimental values of dispersion partial solubility parameter, δ_d (344 data points)

[14]. The tables of the present article contain the contributions to all Hansen solubility parameters so as to give the opportunity for a simultaneous estimation of a complete set of parameters. The information included in all tables of the present article is also available in more accessible formats from the authors upon request.

In cases of low δ_p or low δ_{hb} values (less than 3 MPa$^{(1/2)}$), the equations for the estimation of δ_p and δ_{hb} are the following:

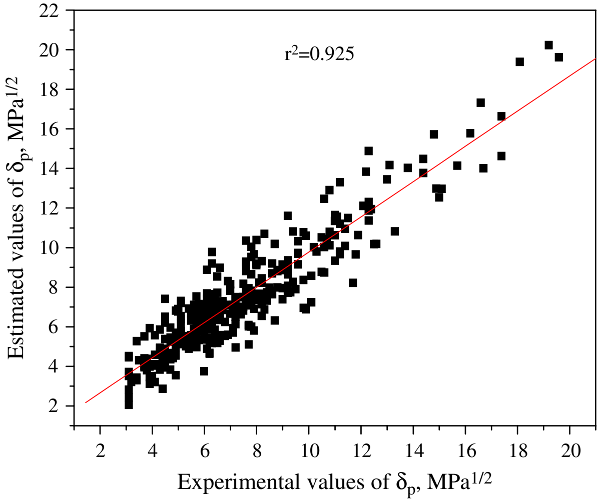

Fig. 2 Correlation between estimated and experimental values of polar partial solubility parameter, δ_{p} (350 data points)

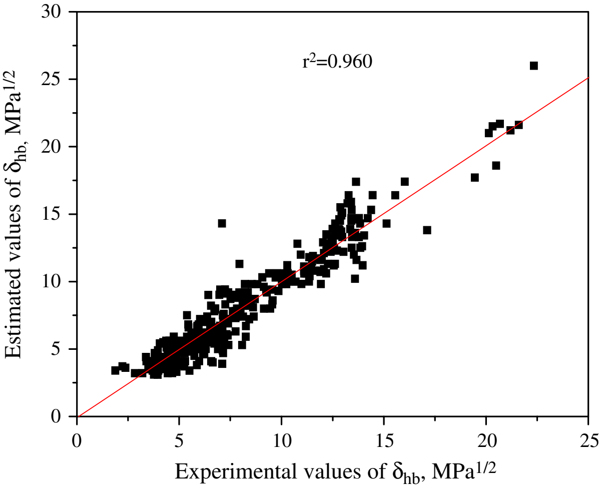

Fig. 3 Correlation between estimated and experimental values of hydrogen-bonding partial solubility parameter, δ_{hb} (375 data points)

$$\delta_{\mathrm{p}} = \left(\sum_i N_i C_i + W \sum_j M_j D_j + 2.7467 \right) \mathrm{MPa}^{(1/2)} \tag{27}$$

$$\delta_{\mathrm{hb}} = \left(\sum_i N_i C_i + W \sum_j M_j D_j + 1.3720 \right) \mathrm{MPa}^{(1/2)} \tag{28}$$

Tables 5 and 6 present the contributions of first-order and second-order groups to δ_p and δ_{hb} when δ_p or δ_{hb} is low.

Hansen solubility parameters of common solvents are reported in the open literature [3,14,15]. The present group-contribution method is particularly useful in the case of compounds for which experimental solubility parameters are not available. Since the molecular structure of these compounds is known, the constituent groups are known, and thus, the Hansen solubility parameters can be predicted using the above equations and tables. In addition, the well-documented suggestion for the synthesis of solvents with desired solubility properties is possible.

The main advantages of our method for the estimation of Hansen solubility parameters are the following:

(i) The estimation of Hansen solubility parameters is achieved directly, by just using a simple equation for each parameter.
(ii) No experimental data are needed for the estimations.
(iii) The large number of first-order and second-order groups ensures the prediction of Hansen solubility parameters for a huge variety of organic compounds, including those having complex molecular structure.

2.4 Example Calculations

2.4.1 1-Hexanal (CH_3CH_2CHO)

The prediction of the Hansen solubility parameters of 1-hexanal using our method is presented in Tables 7–9. Table 10 shows the experimental values, the values estimated by our method, and the values estimated by the Hoy method. The method by Hoftyzer and van Krevelen [7] is not able to estimate the Hansen solubility parameters of 1-hexanal, since the –CHO (aldehydes) group contributions are not available in tables.

2.4.2 1,2-Dihydroxy-9,10-anthracenedione (Alizarin)

An example compound with unknown Hansen solubility parameters is 1,2-dihydroxy-9,10-anthracenedione or *alizarin* (Fig. 4). The knowledge of Hansen solubility parameters of alizarin is of crucial importance for the selection of an appropriate solvent for this compound. A solvent with Hansen solubility parameters very similar to those of alizarin is sought. The estimations of the Hansen solubility parameters of alizarin using our group-contribution method are presented next.

First-order approximation for δ_d ($W = 0$):
First-order approximation value (Table 11):

$$\delta_d = \left(\sum_i N_i C_i + 17.3231\right) = 21.55\,\text{MPa}^{(1/2)}.$$

Second-order approximation for δ_d ($W = 1$):

Table 3 First-order group contributions to the dispersion partial solubility parameter, δ_d, the polar partial solubility parameter, δ_p, and the hydrogen-bonding partial solubility parameter, δ_hb

First-order groups	δ_d	δ_p	δ_hb	Examples (Occurrences)
$-CH_3$	−0.9714	−1.6448	−0.7813	Propane (2)
$-CH_2$	−0.0269	−0.3045	−0.4119	Butane (2)
$-CH<$	0.6450	0.6491	−0.2018	Isobutane (1)
$>C<$	1.2686	2.0838	0.0866	Neopentane (1)
$CH_2{=}CH-$	−1.0585	−2.0035	−1.2985	Propylene (1)
$-CH{=}CH-$	0.0048	−0.2984	−0.0400	*cis*-2-Butene (1)
$CH_2{=}C<$	−0.4829	−0.7794	−0.8260	Isobutene (1)
$-CH{=}C<$	0.5372	−0.9024	−1.8872	2-Methyl-2-butene (1)
$>C{=}C<$	0.3592	1.0526	−15.4659	2,3-Dimethyl-2-butene (1)
$CH_2{=}C{=}CH-$	−1.6518	***	−0.9980	1,2-Butadiene (1)
$CH{\equiv}C-$	0.2320	−1.3294	1.0736	Propyne (1)
$C{\equiv}C$	−0.2028	−0.7598	−1.1083	2-Butyne (1)
ACH	0.1105	−0.5303	−0.4305	Benzene (6)
AC	0.8446	0.6187	0.0084	Naphthalene (2)
$ACCH_3$	0.2174	−0.5705	−1.1473	Toluene (1)
$ACCH_2-$	0.6933	0.6517	−0.1375	*m*-Ethyltoluene (1)
CH_3CO	−0.3551	2.3192	−1.3078	Methyl ethyl ketone (1)
CH_2CO	0.6527	3.7328	−0.5344	Cyclopentanone (1)
CHO (aldehydes)	−0.4030	3.4734	0.1687	1-Butanal (1)
COOH	−0.2910	0.9042	3.7391	Vinyl acid (1)
CH_3COO	−0.5401	−0.3970	1.5826	Ethyl acetate (1)
CH_2COO	0.2913	3.6462	1.2523	Methyl propionate (1)
HCOO	***	1.9308	2.1202	*n*-Propyl formate (1)
COO	0.2039	3.4637	1.1389	Ethyl acrylate (1)
OH	−0.3462	1.1404	7.1908	Isopropanol (1)
ACOH	0.5288	1.1010	6.9580	Phenol (1)
CH_3O	−0.5828	0.1764	0.1460	Methyl ethyl ether (1)
CH_2O	0.0310	0.8826	−0.1528	Ethyl vinyl ether (1)
CHO (ethers)	0.8833	1.6853	0.4470	Diisopropyl ether (1)
$C_2H_5O_2$	−0.1249	3.6422	8.3579	2-Methoxy-ethanol (1)
CH_2O (cyclic)	0.2753	0.1994	−0.1610	1,4-Dioxane (2)
CH_2NH_2	−0.5828	1.4084	2.5920	1-Amino-2-propanol (1)
$CHNH_2$	0.0112	−1.1989	0.3818	Isopropylamine (1)
CH_3NH	***	0.6777	5.6646	*n*-Methylaniline (1)
CH_2NH	0.8116	0.9412	1.3400	di-*n*-Propylamine (1)
CH_3N	0.8769	1.2046	1.6062	Trimethylamine (1)
CH_2N	1.4681	2.8345	1.2505	Triethylamine (1)
$ACNH_2$	1.6987	1.6761	4.5274	Aniline (1)
$CONH_2$	−0.0689	6.0694	5.2280	2-Methacrylamide (1)
$CON(CH_3)_2$	0.4482	5.7899	3.0020	*n,n*-Dimethylacetamide (1)
CH_2SH	1.2797	−0.8223	4.4646	*n*-Butyl mercaptan (1)
CH_3S	***	0.4944	−1.4861	Methyl ethyl sulfide (1)
CH_2S	1.0595	0.7530	−0.2287	Diethyl sulfide (1)
I	0.7797	0.6777	0.2646	Isopropyl iodide (1)
Br	0.5717	0.6997	−1.0722	2-Bromopropane (1)
CH_2Cl	0.2623	0.5970	−0.5364	*n*-Butyl chloride (1)
CHCl	0.4462	2.8060	−1.4125	Isopropyl chloride (1)
CCl	2.7576	2.0406	0.1101	t-Butyl chloride (1)
$CHCl_2$	1.1797	1.8361	−3.2861	1,1-Dichloropropane (1)
CCl_2	0.3653	0.1696	−1.4334	Pentachlorocyclopropane (2)
CCl_3	***	1.2777	−2.6354	Benzotrichloride (1)
ACCl	0.8475	−0.0339	−0.7840	*m*-Dichlorobenzene (2)
ACF	0.1170	0.1856	−0.7182	Fluorobenzene (1)

Table 3 continued

First-order groups	δ_d	δ_p	δ_{hb}	Examples (Occurrences)
Cl–(C=C)	0.2289	2.3444	3.8893	2,3-Dichloropropene (1)
CF_3	−0.2293	−1.9735	−1.4665	Perfluorohexane (2)
CH_2NO_2	***	6.8944	−1.2861	1-Nitropropane (1)
$CHNO_2$	***	8.0347	−2.3167	2-Nitropropane (1)
$ACNO_2$	1.4195	4.4838	−0.7167	Nitrobenzene (1)
CH_2CN	−0.3392	6.5341	−0.8892	*n*-Butyronitrile (1)
CF_2	−0.9729	***	***	Perfluoromethylcyclohexane (5)
CF	0.1707	***	***	Perfluoromethylcyclohexane (1)
F (except as above)	−0.7069	***	***	2-Fluoropropane (1)
$CH_2{=}C{=}C<$	−0.2804	***	−1.9167	3-Methyl-1,2-butadiene (1)
O (except as above)	0.0472	3.3432	0.0256	Divinyl ether (1)
Cl (except as above)	0.2256	1.8711	−0.3295	Hexachlorocyclopentadiene (2)
>C=N–	−0.3074	−0.0012	−5.3956	2,4,6-Trimethylpyridine (1)
−CH=N–	0.9672	1.9728	0.7668	Isoquinoline (1)
NH (except as above)	***	0.0103	2.2086	Dibenzopyrrole (1)
CN (except as above)	0.0861	6.5331	−0.6849	*cis*-Crotonitrile (1)
O=C=N–	−0.1306	1.6102	4.0461	*n*-Butyl isocyanate (1)
SH (except as above)	1.0427	1.9813	4.8181	2-Mercaptobenzothiazole (1)
S (except as above)	1.4899	9.2072	−0.6250	Thiophene (1)
SO_2	1.5502	11.1758	0.1055	Sulfolene (1)
>C=S	0.7747	0.0683	3.4080	*n*-Methylthiopyrrolidone (1)
$>C{=}0$ (except as above)	−0.4343	0.7905	1.8147	Anthraquinone (2)
N (except as above)	1.5438	2.5780	1.1189	Triphenylamine (1)

*** The specific group contributions to this delta parameter are not available

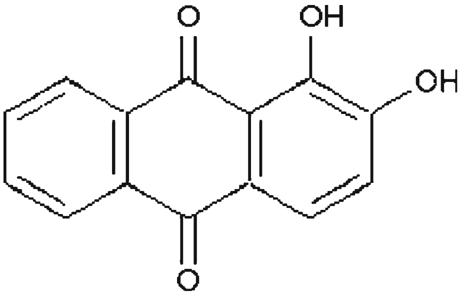

Fig. 4 Chemical formula of 1,2-dihydroxy-9,10-anthracenedione (alizarin)

Second-order approximation value (Table 12):

$$\delta_{\mathrm{d}} = \left(\sum_i N_i C_i + \sum_j M_j D_j + 17.3231 \right) = 20.96\,\mathrm{MPa}^{(1/2)}$$

First-order approximation for δ_p ($W = 0$):
First-order approximation value (Table 13):

$$\delta_{\mathrm{p}} = \left(\sum_i N_i C_i + 7.3548 \right) = 10.43\,\mathrm{MPa}^{(1/2)}.$$

Table 4 Second-order group contributions to the dispersion partial solubility parameter, δ_d, the polar partial solubility parameter, δ_p, and the hydrogen-bonding partial solubility parameter, δ_hb

Second-order groups	δ_d	δ_p	δ_hb	Examples (Occurrences)
$(\mathrm{CH_3})_2$–CH–	0.0460	0.0019	0.3149	Isobutane (1)
$(\mathrm{CH_3})_3$–C–	−0.0738	1.1881	−0.2966	Neopentane (1)
ring of 5 carbons	−0.6681	−2.3430	−0.3079	Cyclopentane (1)
ring of 6 carbons	−0.3874	−3.6432	***	Cyclohexane (1)
−C=C–C=C–	−0.1355	−3.5085	−1.0795	1,3-Butadiene (1)
$\mathrm{CH_3}$-C=	−0.0785	0.3316	0.3875	Isobutene (2)
−$\mathrm{CH_2}$–C=	−0.3236	−2.3179	−0.5836	1-Butene (1)
>C{H or C}–C=	−0.2798	***	−1.1164	3-Methyl-1-butene (1)
string in cyclic	−0.1945	***	***	Ethylcyclohexane (1)
$\mathrm{CH_3(CO)CH_2}$–	−0.0451	−0.3383	−0.4083	Methyl ethyl ketone (1)
$\mathrm{C_{cyclic}}$=O	−0.2981	0.4497	−0.4794	Cyclopentanone (1)
ACCOOH	−0.2293	−0.6349	−0.9030	Benzoic acid (1)
>C{H or C}–COOH	***	−0.2187	1.1460	Isobutyric acid (1)
CH3(CO)OC{H or C}<	−0.5220	−0.0652	0.3085	Isopropyl acetate (1)
(CO)C{$\mathrm{H_2}$}COO	***	−2.3792	0.8412	Ethyl acetoacetate (1)
(CO)O(CO)	−0.2707	−1.0562	1.6335	Acetic anhydride (1)
ACHO	0.3772	−1.8110	−1.0096	Benzaldehyde (1)
>CHOH	0.1123	0.2564	−0.1928	2-Propanol (1)
>C<OH	−0.0680	0.1075	1.2931	Tert-Butanol (1)
−C(OH)C(OH)–	***	0.6419	0.3870	1,2-Propanediol (1)
−C(OH)C(N)	−0.0809	0.5683	−0.6326	1-Amino-2-propanol (1)
$\mathrm{C_{cyclic}}$–OH	−0.0876	−3.5220	0.5914	Cyclohexanol (1)
C–O–C=C	0.2063	0.6080	1.1344	Ethyl vinyl ether (1)
AC–O–C	0.2568	0.8153	0.6092	Methyl phenyl ether (1)
>N{H or C}(in cyclic)	0.2218	−2.2018	−0.0452	Cyclopentimine (1)
−S-(in cyclic)	0.4892	0.3040	0.2297	Tetrahydrothiophene (1)
ACBr	0.1234	−0.4495	0.3397	Bromobenzene (1)
(C=C)–Br	−0.4059	−0.0024	−1.1304	2-Bromopropene (1)
ring of 3 carbons	0.0200	1.8288	−0.8073	Cyclopropane (1)
ACCOO	−0.1847	0.4059	−0.1921	Methyl benzoate (1)
$\mathrm{AC(ACH}_m)_2\mathrm{AC(ACH_n)_2}$	−0.3751	−1.2980	0.6844	Naphthalene (1)
$\mathrm{O_{cyclic}}$–$\mathrm{C_{cyclic}}$=O	0.2468	2.7501	0.1220	Diketene (1)
AC–O–AC	−0.5646	−3.4329	2.0830	Diphenyl ether (1)
$\mathrm{C_{cyclic}H}_m$=$\mathrm{N_{cyclic}}$–$\mathrm{C_{cyclic}H}_n$=$\mathrm{C_{cyclic}H_p}$	0.7002	0.0691	−2.7661	2,6-Dimethylpyridine (1)
$\mathrm{N_{cyclic}H}_m$–$\mathrm{C_{cyclic}}$=O	0.2956	2.8958	1.3125	2-Pyrrolidone (1)
−O–CH_m–O–CH_n–	0.0839	0.3451	0.3767	Methylal (1)
C(=O)–C–C(=O)	−0.4862	−0.4888	1.2482	2,4-Pentanedione (1)

*** The specific group contributions to this delta parameter are not available

Second-order approximation for δ_p ($W=1$):
Second-order approximation value (Table 14):

$$\delta_\mathrm{p} = \left(\sum_i N_i C_i + \sum_j M_j D_j + 7.3548\right) = 11.33\,\mathrm{MPa}^{(1/2)}.$$

Table 5 First-order group contributions to the polar partial solubility parameter, δ_p (low δ_p values, $\delta_p < 3\ (\mathrm{MPa})^{0.5}$), and the hydrogen-bonding partial solubility parameter, δ_{hb} (low δ_{hb} values, $\delta_{hb} < 3\ (\mathrm{MPa})^{0.5}$)

First-order groups	Low δ_p	Low δ_{hb}
$-CH_3$	−0.72412	0.29901
$-CH_2$	−0.14030	−0.11610
$-CH<$	0.58978	0.1386
$CH_2{=}CH-$	−0.29774	1.35521
$-CH{=}CH-$	−0.22864	0.48189
$CH_2{=}C<$	0.64816	0.11148
$-CH{=}C<$	1.22566	−0.03066
$>C{=}C<$	***	−0.12117
$CH_2{=}C{=}CH-$	−0.32258	***
$CH{\equiv}C-$	−0.74895	0.43846
$C{\equiv}C$	***	−0.35107
ACH	−0.19313	0.13532
AC	0.16369	−0.17405
$ACCH_3$	−0.47724	−0.28733
$ACCH_2-$	−0.33086	−0.88084
$ACCH<$	0.86718	−1.44666
CH_3COO	1.71923	***
CH_2COO	2.16274	***
COO	1.60913	0.37204
OH	1.84013	***
CH_3O	−0.40320	***
CH_2O	***	***
CHO	***	−0.40667
CH_2O (cyclic)	−0.33305	***
CH_2NH_2	***	***
CH_2NH	0.83214	***
CHNH	1.25999	***
CH_3N	***	−0.17004
CH_2N	0.65229	−1.03686
CH_2S	***	0.14606
CH_2Cl	***	0.48952
CHCl	***	0.12996
$CHCl_2$	***	0.52541
ACCl	−0.10778	0.44238
CCl_2F	***	***
ACF	***	−0.37183
Cl–(C=C)	***	0.66062
CF_3	***	−0.08871
$CH_2{=}C{=}C<$	1.20154	***
O (except as above)	−0.48942	***
Cl (except as above)	***	1.12515
S (except as above)	0.11058	***
$>C{=}0$ (except as above)	***	−0.05529

*** The specific group contributions to this delta parameter are not available

First-order approximation for δ_{hb} ($W{=}0$):
First-order approximation value (Table 15):

$$\delta_{hb} = \left(\sum_i N_i C_i + 7.9793\right) = 22.9753\,(\mathrm{MPa})^{(1/2)}.$$

Table 6 Second-order group contributions to the polar partial solubility parameter, δ_p (low δ_p values, $\delta_p < 3\ (\mathrm{MPa})^{0.5}$), and the hydrogen-bonding partial solubility parameter, δ_{hb} (low δ_{hb} values, $\delta_{hb} < 3\ (\mathrm{MPa})^{0.5}$)

Second-order groups	Low δ_p	Low δ_{hb}
$(CH3)_2$–CH–	0.200694	10^{-8}
Ring of 5 carbons	−0.897912	0.19438
Ring of 6 carbons	−0.956852	$2\ 10^{-8}$
–C=C–C=C–	0.648793	***
CH_3–C=	−0.008375	−0.061370
–CH_2–C=	0.011009	0.06599
>C{H or C}–C=	−0.39720	0.342229
String in cyclic	***	−0.280859
ACCOO	0.491153	10^{-8}
$AC(ACH_m)_2AC(ACHn)_2$	0.013012	0.086424
–O–CH_m–O–CH_n–	0	***

*** The specific group contributions to this delta parameter are not available

Table 7 First-order group approximation for the prediction of the dispersion partial solubility parameter, δ_d, of 1-hexanal

1st-Order groups	Occurrences, N_i	Contributions, C_i	$N_i C_i$
–CH_3	1	−0.9714	−0.9714
–CH_2	4	−0.0269	−0.1076
–CHO (aldehydes)	1	−0.4030	−0.4030
Constant, C			17.3231
$\Sigma N_i C_i + C$			15.8411

Table 8 First-order group approximation for the prediction of the polar partial solubility parameter, δ_p, of 1-hexanal

1st-Order groups	Occurrences, N_i	Contributions, C_i	$N_i C_i$
–CH_3	1	−1.6448	−1.6448
–CH_2	4	−0.3045	−1.2180
–CHO (aldehydes)	1	3.4734	3.4734
Constant, C			7.3548
$\Sigma N_i C_i + C$			7.9654

Table 9 First-order group approximation for the prediction of the hydrogen-bonding partial solubility parameter, δ_{hb}, of 1-hexanal

1st-Order groups	Occurrences, N_i	Contributions, C_i	$N_i C_i$
–CH_3	1	−0.7813	−0.7813
–CH_2	4	−0.4119	−1.6476
–CHO (aldehydes)	1	0.1687	0.1687
Constant, C			7.9793
$\Sigma N_i C_i + C$			5.7191

Table 10 Experimental and estimated (by Stefanis method and Hoy method) partial solubility parameters for 1-hexanal

	Hansen [15]	Stefanis	Hoftyzer	*Hoy*
δ_d in $(\mathrm{MPa})^{0.5}$	15.8	15.8	–	14.7
δ_p in $(\mathrm{MPa})^{0.5}$	8.5	8.0	–	8.1
δ_{hb} in $(\mathrm{MPa})^{0.5}$	5.4	5.7	–	12.8

Table 11 First-order group approximation for the prediction of the dispersion partial solubility parameter, δ_{d}, of alizarin

1st-Order groups	Occurrences, N_i	Contributions, C_i	$N_i C_i$
ACH	6	0.1105	0.6630
AC	4	0.8446	3.3784
ACOH	2	0.5288	1.0576
$>C=0$ (except as above)	2	−0.4343	−0.8686
Constant, C			17.3231
$\Sigma \mathrm{N}_i \mathrm{C}_i+\mathrm{C}$			21.5535

Table 12 Second-order group approximation for the prediction of the dispersion partial solubility parameter, δ_{d}, of alizarin

2nd-Order groups	Occurrences, M_j	Contributions, D_j	$M_j D_j$
C(cyclic)=O	2	−0.2981	−0.5962

Table 13 First-order group approximation for the prediction of the polar partial solubility parameter, δ_{p}, for alizarin

1st-Order groups	Occurrences, N_i	Contributions, C_i	$N_i C_i$
ACH	6	−0.5303	−3.1818
AC	4	0.6187	2.4748
ACOH	2	1.1010	2.202
$>C=0$ (except as above)	2	0.7905	1.581
Constant, C			7.3548
$\Sigma \mathrm{N}_i \mathrm{C}_i+\mathrm{C}$			10.4308

Table 14 Second-order group approximation for the prediction of the polar partial solubility parameter, δ_{p}, for alizarin

2nd-Order groups	Occurrences, M_j	Contributions, D_j	$M_j D_j$
C(cyclic)=O	2	0.4497	0.8994

Table 15 First-order group approximation for the prediction of the hydrogen-bonding partial solubility parameter, δ_{hb}, for alizarin

1st-Order groups	Occurrences, N_i	Contributions, C_i	$N_i C_i$
ACH	6	−0.4305	−2.583
AC	4	0.0084	0.0336
ACOH	2	6.9580	13.916
$>C=0$ (except as above)	2	1.8147	3.6294
Constant, C			7.9793
$\Sigma \mathrm{N}_i C_i + C$			22.9753

Second-order approximation for δ_{hb} ($W=1$):
Second-order approximation value (Table 16):

$$\delta_{\mathrm{hb}} = \left(\sum_i N_i C_i + \sum_j M_j D_j + 7.9793 \right) = 22.02\,(\mathrm{MPa})^{(1/2)}.$$

Table 16 Second-order group approximation for the prediction of the hydrogen-bonding partial solubility parameter, δ_{hb}, for alizarin

2nd-Order groups	Occurrences, M_j	Contributions, D_j	$M_j D_j$
C(cyclic)=O	2	−0.4794	−0.9588

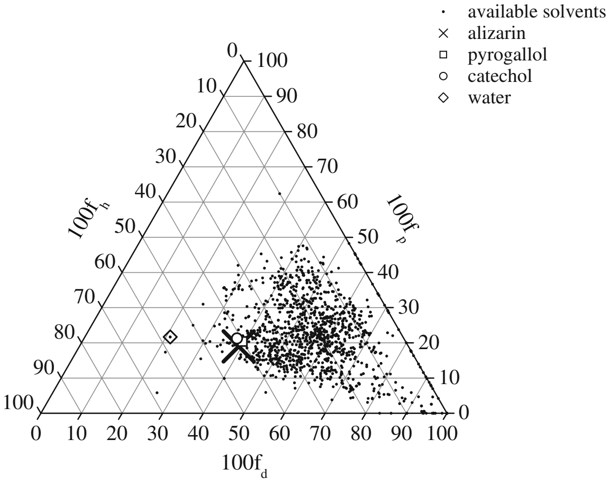

Fig. 5 Teas ternary plot. The position of alizarin is shown with an "X", the positions of common solvents are shown with small, scattered spots, the position of pyrogallol with a square, the position of catechol with a circle and the position of water with a diamond

One method for finding the best solvents for alizarin is by calculating the R_a distance between alizarin and the solvents included in the handbook of Hansen [15]. Using Eq. 5, it is calculated that the smallest R_a distance (1.23) is between alizarin and 1,2,3-trihydroxybenzene (pyrogallol). The second smallest R_a distance (1.93) is between alizarin and 1,2-dihydroxybenzene (catechol). Thus, pyrogallol and catechol are the two best solvents for alizarin.

A second method for finding solvents for alizarin is using the Teas parameters. Figure 5 shows a Teas ternary plot in which the positions of available common solvents (which were found using their experimental [15] Hansen solubility parameter values) are shown with small, scattered spots.

Using the three estimated solubility parameters, the position of alizarin in the Teas ternary plot can also be found: it is marked in Fig. 5 with an "X." The closest solvent compounds to alizarin are 1,2,3-trihydroxybenzene or pyrogallol (presented with a square in the plot) and 1,2-dihydroxybenzene or catechol (presented with a circle). That means that according to Teas parameters, pyrogallol and catechol are the most appropriate solvents for alizarin from the available common ones. The insolubility of alizarin in water is expressed by the much bigger distance between the positions of the two compounds in the Teas ternary plot.

For the synthesis of an ideal solvent for alizarin, the three estimated Hansen solubility parameters can be fed into an especially developed algorithm, similar to that presented in the literature [16], and a list of additional candidate solvents could be obtained. These solvents, if not available commercially, could be synthesized in the laboratory.

3 Conclusions

With the group-contribution method which was introduced in the present study, the direct prediction of Hansen solubility parameters of organic compounds is possible. The solubility parameter values are calculated using simple linear equations. Only the molecular structures of the compounds are required for the predictions, and no experimental data are needed. The method can be used to predict the Hansen solubility parameters of a broad series of organic compounds with three or more carbon atoms. Using the predicted solubility parameter values, the selection of appropriate solvents for each given solute is possible. By calculating the R_a distances or by constructing a Teas parameter ternary plot, the best existing solvents for each solute can be found. Furthermore, using an especially designed algorithm, it is possible to obtain a list of new molecular structures which, if synthesized, could be the ideally suited solvents for the corresponding application.

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