

# Prediction of Solubility Parameters Using the Group-Contribution Lattice-Fluid Theory

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**ABSTRACT:** A formulation for the solubility parameter based on the group-contribution, lattice fluid equation of state was derived. The solubility parameters of pure liquid solvents, polymers, copolymers, and liquid mixtures were calculated and compared against the best available data. This investigation was conducted on pure components and mixtures of alkanes, alkenes, ketones, ethers, acetates, alcohols, chlorinated molecules, and cyclic and aromatic solvents. The capabilities of the model to distinguish between two isomers and to predict the solubility parameter of supercritical fluids and their mixtures were also studied. The predicted values are generally good, although the error increases when hydrogen bonding is present. A primary application of the procedure is for the prediction of the solubility parameters of polymers. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 197–206, 2001

**Key words:** solubility parameters; polymers; supercritical fluids; mixtures; group contribution; equation of state

## INTRODUCTION

Polymer–polymer and polymer–solvent compatibility are very often approached qualitatively by a comparison of the solubility parameters. The solubility parameter is equal to the square root of the cohesive energy density. The closer the solubility parameters, the more compatible are the compounds to be mixed. Although this concept is more than four decades old, it is still widely used in polymer-related areas such as paints, resins,<sup>1</sup> and medically related molecules.<sup>2</sup>

For a liquid, the molar cohesive energy,  $\Delta U$ , can be interpreted as the contribution of two terms—the molar energy of vaporization,  $\Delta U_v$ , and the energy to expand the saturated vapor to infinite volume at constant temperature,  $\Delta U_\infty$ :

$$\Delta U = \Delta U_v + \Delta U_\infty \quad (1)$$

If the saturated vapor is assumed to be an ideal gas, the second term of eq. (1) is equal to zero. Using the relations between the internal energy and the enthalpy, and assuming the gas of the liquid vapor equilibrium to be ideal, yields

$$\Delta U = \Delta H_v - RT + P_s V^l \quad (2)$$

where  $\Delta H_v$  is the molar heat of evaporation;  $P_s$ , the saturation vapor pressure at temperature  $T$ ; and  $R$ , the gas constant. At pressures below atmospheric pressure, the term  $P_s V^l$  is negligible compared with the other terms and the cohesive energy is approximated with the two first terms of eq. (2). This approximation, however, is not valid at higher pressures.

Since polymers cannot be vaporized, the solubility parameter of polymers can only be determined indirectly. Several techniques have been

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developed such as using the refractive index,<sup>3</sup> the intrinsic viscosity,<sup>4</sup> turbidic titration,<sup>5</sup> inverse gas chromatography,<sup>6,7</sup> or solvent swelling.<sup>8,9</sup> In addition, a number of group-contribution methods have been developed to calculate the solubility parameters of liquids.<sup>10</sup> These methods, such as the one developed by Van Krevelen,<sup>11</sup> are exclusively limited to the prediction of the solubility parameters at 25°C.

An alternative method for calculating solubility parameters is through the use of an equation of state. Panayiotou<sup>12</sup> used the Sanchez–Lacombe EOS and its extension to hydrogen-bonded systems.<sup>13</sup> Similarly, the group-contribution, lattice-fluid theory (GCLF) expresses explicitly the cohesive energy as the sum of the molecular interactions. The density is then obtained from the equation of state, thus allowing the calculation of the solubility parameters. The only information needed for any fluid is its molecular structure. The objective of this work was to evaluate the capabilities and limitations of the GCLF theory for the prediction of the solubility parameter of polymers, pure liquids, supercritical fluids, and their mixtures.

## THEORY

### Pure Components

The GCLF theory is based on the equation of state of Panayiotou and Vera,<sup>14</sup> which is built on the lattice formulation. The lattice sites can be occupied (by molecules) or vacant, making the theory applicable to compressible fluids. Each site of the lattice has a fixed volume ( $v_h = 9.75 \times 10^{-6} \text{ m}^3$ ) and neighboring sites ( $z = 10$ ). Each molecule occupies  $r$  sites and has  $zq$  sites available for interaction expressed as

$$zq = (z - 2)r + 2 \quad (3)$$

Molecules are characterized by their hard-core volume,  $v^*$ , and an interaction energy,  $\varepsilon^*$ . The group-contribution method developed by High and Danner<sup>15</sup> and revised by Lee and Danner<sup>16</sup> assumes that the molecular behavior is the sum of the contributions of the different groups that compose the molecule. The general expression of the canonical partition function is written as

$$Q = \left( \frac{\xi_1}{\sigma_1} \right)^{N_1} g_c g_{nr} \exp\left( \frac{-E}{RT} \right) \quad (4)$$

$\xi_1$  and  $\sigma_1$  are the flexibility and symmetry parameters, respectively;  $g_c$ , the random combinatorial term; and  $g_{nr}$ , the nonrandom combinatorial term for  $N_1$  molecules in the lattice. For a pure fluid, the holes are assumed to be randomly distributed in the lattice and  $g_{nr}$  is equal to 1. The term  $E$  expresses the total interaction energy of the molecules with their nearest neighboring sites. The equation of state is derived from eq. (1) as

$$\frac{\tilde{p}}{\tilde{T}} = \ln\left( \frac{\tilde{v}}{\tilde{v} - 1} \right) + \frac{z}{2} \ln\left( \frac{\tilde{v} + q/r - 1}{\tilde{v}} \right) - \frac{\theta^2}{\tilde{T}} \quad (5)$$

where  $\tilde{P}$ ,  $\tilde{T}$  and  $\tilde{v}$  are the reduced pressure, temperature, and molar volume, respectively:

$$\tilde{P} = P/P^* \quad \tilde{T} = T/T^* \quad \tilde{v} = v/v^*$$

$$0 = \frac{q/r}{\tilde{v} + q/r - 1} \quad (6)$$

and

$$P^* = z\varepsilon^*/2v_h \quad T^* = z\varepsilon^*/2R \quad v^* = v_h r \quad (7)$$

Mixing rules involving the different groups composing molecules are used to obtain the scaling parameters  $\varepsilon^*$  and  $v^*$ . They are expressed as a quadratic expression of temperature. The parameters of these equations are fitted from the liquid–vapor equilibrium of the pure fluids. Lee and Danner<sup>16</sup> gave detailed equations and fitting procedures.

The solubility parameter  $\delta$  is equal to the square root of the cohesive energy density, that is, the square root of cohesive energy per unit of volume  $V$ . The cohesive energy is explicitly expressed by the energy of the lattice  $E$ :

$$\delta = (E/V)^{1/2} \quad (8)$$

where

$$E = N_{11}\varepsilon^* \quad (9)$$

Here,  $N_{11}$  is the total number of interactions in the fluid:

$$N_{11} = \frac{zqN}{2} \theta \quad (10)$$

The total volume of the system is a function of the total number of lattice sites  $N_r$  and of the volume of a site:

$$V = N_r v_h \quad (11)$$

The expression of the solubility parameter is, therefore,

$$\delta = \left( \frac{qP^*\theta}{r\bar{v}} \right)^{1/2} \quad (12)$$

### Mixtures

For mixtures, the nonrandom distribution of the molecules is expressed through the nonrandom combinatorial term  $g_{nr}$  obtained from the quasichemical approximation of Guggenheim. Mixing rules must be applied to the scaling parameters. They are defined as

$$v^* = x_1 v_1^* + x_2 v_2^* \quad (13)$$

$$\varepsilon_{12}^* = (\varepsilon_{11}^* \varepsilon_{22}^*)^{1/2} (1 - k_{12}) \quad (14)$$

where  $\varepsilon_{12}^*$  is the interaction energy between unlike molecules, and  $k_{12}$ , the interaction parameter. The derivation of the equation of state for the mixture leads to an overall interaction energy expressed as

$$\varepsilon^* = \bar{\theta}_1 \varepsilon_1^* + \bar{\theta}_2 \varepsilon_2^* - \bar{\theta}_1 \bar{\theta}_2 \dot{\Gamma}_{12} \Delta\varepsilon \quad (15)$$

where

$$\Delta\varepsilon = \varepsilon_{11}^* + \varepsilon_{22}^* - 2\varepsilon_{12}^* \quad (16)$$

$\dot{\Gamma}_{12}$  is the nonrandomness parameter resulting from the nonrandom combinatorial term and  $\bar{\theta}_i$  is the surface area fraction of component  $i$  on a hole-free basis.

The expression of the solubility parameter remains the same. Since the holes are randomly distributed, the equation of state of the mixture remains the same as that of the pure fluid.

## RESULTS AND DISCUSSION

### Pure Fluids

Barton<sup>11</sup> provided two solubility parameter tables: the Hildebrand solubility parameters

adapted from Burell<sup>17</sup> and the Hildebrand and Hanson solubility parameters (also called Hanson 3D solubility parameters) adapted from the Union Carbide Corp.<sup>18</sup> Table I compares the experimental Hildebrand and Hanson 3D solubility parameters, those given in the database of Daubert et al.,<sup>19</sup> and the solubility parameters predicted by the GCLF-EOS. The experimental and database values are in good agreement. The data reported by Burell<sup>17</sup> and the Union Carbide table<sup>18</sup> for, respectively, *n*-decane and 1-butanol, however, do not follow the trends. The values obtained from the database are estimated from the heat of evaporation and the density of the pure fluids, which are fitted over the best available data in the literature. For consistency, the predicted solubility parameters are compared against those obtained from the database of Daubert et al.,<sup>19</sup> which treats the widest number of solvents.

As shown in Table I, the solubility parameters of *n*-alkanes and *n*-alkenes increases with the molecular weight. This trend is well reproduced by the GCLF-EOS, which overestimates the solubility parameters. The relative error decreases, however, with increasing chain length and is, in all cases, less than 7%. The predicted values consistently overpredict the experimental data by 5–6% on average.

In comparison with *n*-alkane, the slightly and strongly hydrogen-bonding solvents have a high solubility parameter due to the strong interactions induced by the carbonyl and the hydroxyl groups. Moreover, the solubility parameter of ketones and alcohols decreases with the molecular weight, opposite to the trend observed for *n*-alkanes. This behavior can be caused either by a decrease of the molar cohesive energy or by a decrease of the density. For these solvents, the density increases with the molecular weight. The observed significant decrease in the solubility parameter with the molecular weight is therefore solely caused by the decrease of the cohesive energy. As the chain length increases, the surface area fraction of the strongly interacting groups decreases. The probability of interaction with these groups decreases, leading to a decrease in the cohesive energy that tends toward the value of the corresponding *n*-alkane. The GCLF-EOS reproduces this behavior.

The Panayiotou-Vera<sup>14</sup> model for pure fluids does not take into account hydrogen bonding and assumes a random distribution of the holes in the lattice. The large negative discrepancy for alco-

**Table I Solubility Parameter of Pure Fluids from Different References at 298.15 K Compared to Those Obtained by the GCLF-EOS**

	$\delta$ (Ref. 19)	$\delta$ (Ref. 17)	$\delta$ (Ref. 18)	GCLF	% Error
<u>Alkanes</u>					
<i>n</i> -Butane	13.70	13.9	13.5	14.53	6.1
<i>n</i> -Pentane	14.40	14.3	14.4	15.32	6.4
<i>n</i> -Hexane	14.90	14.9	14.9	15.76	5.8
<i>n</i> -Heptane	15.20	15.1	15.3	15.98	5.1
<i>n</i> -Octane	15.40	15.6	15.4	16.31	5.9
<i>n</i> -Nonane	15.60	—	15.6	16.49	5.7
<i>n</i> -Decane	15.70	13.5 <sup>a</sup>	15.8	16.64	6.0
<i>n</i> -Undecane	15.90	—	16.0	16.76	5.4
<i>n</i> -Dodecane	16.00	16.2	16.2	16.86	5.4
<i>n</i> -Tridecane	16.00	16.4	16.4	16.95	5.9
2-Methylpentane	14.40	—	14.4	15.51	7.7
2-2-Dimethylpentane	14.26	—	14.1	15.46	8.4
2,3-Dimethylpentane	14.82	—	14.8	15.65	5.6
2,2,3-Trimethylpentane	14.69	—	14.7	15.58	6.1
2,3,4-Trimethylpentane	14.94	—	—	15.68	5.0
2,2,3,3-Tetramethylpentane	15.06	—	15.2	15.60	3.6
Average error					5.9
<u>Alkenes</u>					
1-Butene	13.66	—	13.6	14.52	6.3
1-Pentene	14.48	14.1	14.5	15.24	5.2
1-Hexene	15.01	15.1	15.1	15.72	4.7
1-Heptene	15.32	—	15.3	16.05	4.8
1-Octene	15.51	—	15.5	16.29	5.0
1-Nonene	15.72	—	15.8	16.48	4.8
1-Decene	15.82	—	16.0	16.63	5.1
<i>trans</i> -2-Pentene	14.97	—	15.0	15.48	3.4
<i>cis</i> -2-Hexene	15.32	—	15.2	15.91	3.9
<i>cis</i> -2-Heptene	15.37	—	15.4	16.21	5.5
<i>cis</i> -2-Octene	15.50	—	15.5	16.43	6.0
2-Methyl-1-pentene	15.07	—	14.9	15.83	5.0
3-Methyl-1-pentene	14.44	—	14.5	15.48	7.2
4-Methyl-1-pentene	14.48	—	15.3	15.48	6.9
2,3-Dimethyl-1-butene	14.62	—	14.7	15.55	6.4
Average error					5.4
<u>Ketones</u>					
Acetone	19.73	20.2	20.2	18.67	-5.4
Methyl ethyl ketone	18.88	19.0	19.0	18.54	-1.8
2-Pentanone	18.29	17.8	18.4	18.46	0.9
2-Heptanone	17.80	17.4	18.4	18.35	3.1
2-Nonanone	17.56	—	16.8	18.21	3.7
3-Pentanone	18.41	18.0	18.5	18.11	-1.6
3-Hexanone	17.93	—	17.6	18.10	0.9
3-Heptanone	17.94	—	17.4	18.00	0.3
2,6-Dimethyl-4-heptanone	16.54	16.0	16.5	17.71	7.1
Average error					2.8
<u>Acetates</u>					
Methyl acetate	19.35	19.6	19.4	17.62	-8.9
Ethyl acetate	18.35	18.6	18.2	17.70	-3.5
<i>n</i> -Propyl acetate	17.89	18	18	17.74	-0.8

Table I Continued

	$\delta$ (Ref. 19)	$\delta$ (Ref. 17)	$\delta$ (Ref. 18)	GCLF	% Error
<u>Acetates</u>					
<i>n</i> -Butyl acetate	17.67	17.4	17.8	17.78	0.6
<i>n</i> -Pentyl acetate	17.36	17.4	—	17.83	2.7
Isopropyl acetate	17.15	17.2	17.6	17.53	2.2
Isobutyl acetate	17.05	17	17.2	17.60	3.2
Average error					3.2
<u>Alcohols</u>					
Methanol	29.59	29.6	29.7	25.55	-13.7
Ethanol	26.14	26.0	26.1	22.24	-14.9
1-Propanol	24.45	24.3	24.9	21.32	-12.8
1-Butanol	23.35	23.3	28.7 <sup>a</sup>	20.73	-11.2
1-Pentanol	22.52	22.3	22.7	20.31	-9.8
1-Hexanol	21.83	21.9	22.0	20.01	-8.3
1-Heptanol	21.54	21.7	21.5	19.77	-8.2
1-Octanol	21.02	21.1	21.1	19.58	-6.9
1-Decanol	20.25	20.5	20.5	19.31	-4.6
1-Dodecanol	19.75	20.1	20.0	19.11	-3.2
2-Butanol	22.62	22.1	22.7	21.04	-7.0
2-Octanol	20.13	—	19.1	19.44	-3.4
2-Ethy-1-butanol	20.90	21.5	21.2	19.83	-5.1
Benzyl alcohol	24.70	24.8	24.6	23.74	-3.9
Cyclohexanol	23.73	23.3	22.3	21.50	-9.4
Average error					8.2
<u>Ethers</u>					
Diethyl ether	15.42	15.10	15.4	15.71	1.9
Di- <i>n</i> -propyl ether	15.6	16.0	16.0	16.3	4.8
Di( <i>n</i> -hexyl) ether	16.47	16.40	16.4	17.09	3.8
Ethyl propyl ether	15.41	—	—	16.01	3.9
Ethyl butyl ether	15.70	—	15.7	16.30	3.8
Diisopropyl ether	14.45	14.10	14.1	15.78	9.2
Ethyl isobutyl ether	14.8	15.3	15.3	16.1	8.8
Vinyl butyl ether	16.46	—	16.1	16.41	-0.3
Average error					4.6
<u>Cyclic + aromatic</u>					
Cyclopentane	16.55	17.8	16.5	17.16	3.7
Cyclohexane	16.76	16.8	16.8	17.20	2.6
<i>cis</i> -1,2-					
Dimethylcyclopentane	16.16	—	15.4	16.59	2.7
1,1-Dimethylcyclohexane	15.67	—	15.7	16.44	4.9
Ethylcyclopentane	16.25	—	16.2	17.01	4.7
Ethylcyclohexane	16.34	—	16.3	17.05	4.3
<i>n</i> -Butyl cyclopentane	16.39	—	16.4	17.24	5.2
<i>n</i> -Butyl cyclohexane	16.4	—	16.2	17.25	5.2
Benzene	18.7	18.8	18.7	18.73	0.2
Toluene	18.25	18.2	18.3	18.70	2.5
Ethyl benzene	17.95	18	18.1	18.33	2.1
<i>n</i> -Propylbenzene	17.67	17.6	17.6	18.28	3.5
<i>n</i> -Butylbenzene	17.51	—	17.5	18.25	4.2
Average error					3.5

Table I Continued

	$\delta$ (Ref. 19)	$\delta$ (Ref. 17)	$\delta$ (Ref. 18)	GCLF	% Error
<u>Chlorinated</u>					
Dichloromethane	20.37	20.3	20.3	19.59	-3.8
Chloroform	18.92	19.0	18.7	18.78	-0.7
Carbon tetrachloride	17.55	17.6	17.8	17.95	2.3
1,1-Dichloroethane	18.30	—	18.3	18.23	-0.4
1,2-Dichloroethane	20.26	—	20.2	20.01	-1.2
1,1,2-Trichloroethane	19.89	19.6	20.9	20.23	1.7
1,1,1-Trichloroethane	17.25	—	—	17.63	2.2
1,1,2,2-Tetrachloroethane	19.95	19.8	—	20.54	3.0
1-Chloropropane	17.08	17.4	17.2	17.11	0.2
1,2-Dichloropropane	18.4	18.4	—	18.66	1.4
Pentachloroethane	18.98	19.2	—	19.82	4.4
Chlorobenzene	19.35	19.4	18.7	19.56	1.1
Chlorotoluene( <i>para</i> )	19.29	18.0	—	19.39	0.5
Dichlorobenzene( <i>o</i> )	20.31	20.5	20.5	20.14	-0.8
Average error					1.7

<sup>a</sup> Inconsistent value.

The error is against the data from ref. 19.

hols is therefore expected. For ketones and acetates, the error is large only for lower molecular weights. The errors, however, do not exceed 10%. As the molecular weight increases, the error drops below 5%. The GCLF-EOS theory predictions agree with the experimental values for ethers although they are classified as slightly hydrogen-bonding solvents. The fact that the ether group is not as accessible as are the ketone and acetate groups could be the reason. One exception from this trend is diisopropyl ether for which the solubility parameter is significantly overpredicted. Two bulky isopropyl groups surround the oxygen atom, reducing its accessibility for interaction. Since the estimation of the pure fluids' parameters takes into account only the groups, steric exclusion is not accounted for, resulting in an overestimation of the cohesive energy.

The ability of the model to differentiate between isomers was tested. It was successful for cases where strong changes in the solubility parameter are found, such as for 1,1-dichloroethane/1,2-dichloroethane, 1,1,1-trichloroethane/1,1,2-trichloroethane, as well as *n*-alkane isomers that have small changes in the solubility parameter. However, the theory fails to predict the influence of the functional group in *n*-alcohols and *n*-ketones. The error is generally lower when the functional group is on a carbon that is not at the end of the molecule. The steric exclusion effects can

explain the decrease of the solubility parameter and the better prediction. When the hydroxyl group is at the end of the chain, it has a higher accessibility for interactions. Since the model underestimates the hydrogen-bonding interactions, better agreement for molecules having the least hydrogen bonding is expected.

The GCLF-EOS shows similar accuracy for cyclic molecules and *n*-alkanes, which is expected considering the similar molecular composition. Aromatics are likely to be polar and chlorinated molecules may be very polar due to the strong electronegative characteristic of chlorine. The predictions of the GCLF-EOS are, in both cases, satisfactory even for highly chlorinated molecules such as pentachloroethane. Lee<sup>20</sup> showed that the GCLF-EOS gives good density predictions for fluids of different natures over a wide range of temperature. The cohesive energy, that is, the total interactions in the fluid, is therefore well accounted for by the GCLF theory for polar systems.

The solubility parameters of polymers and copolymers found in the literature are scattered over a wide range due to the indirect and different methods used for the measurements. For a given method, the results may differ because of the use of solvents of different hydrogen-bonding capability. In other cases, solubility parameters are obtained using chromatography, in combination with a thermodynamic model.<sup>21</sup> Table II com-

**Table II Solubility Parameters of Polymers and Copolymers at 298.15 K Compared with the Predictions of the GCLF-EOS**

Polymers	$\delta$ (Ref. 17)	$\delta$ (Ref. 22)	$\delta$ (Ref. 11)	GCLF
Poly(vinyl chloride)	19.0–22.7	21.5	19.22–22.09	20.52
Polyisobutylene	14.5–17.0	15.5	15.95–16.57	16.95
Poly(methyl methacrylate)	18.61–26.8	22.7	18.61–26.18	19.39
Polystyrene	15.6–21.1	22.5	17.39–19.02	20.48
Poly(vinyl acetate)	17.4–30.0	25.7	19.1–22.6	20.41
Poly(dimethyl siloxane)	—	—	14.93–15.54	14.31
Poly(tetrafluoroethylene)	—	—	12.68	16.14
Polybutadiene	—	—	16.57–17.59	15.09
Poly(propylene oxide)	—	—	15.34–20.25	17.5
Polyethylene	15.76–17.99	—	15.75–17.8	17.97
50/50 Poly(methyl methacrylate- co-ethyl acrylate)	16.0–27.0	—	—	19.68
25/75 Poly(methyl methacrylate- co-ethyl acrylate)	18.2–29.7	—	—	19.83
85/15 Poly(styrene-co-methyl acrylate)	16–22.7	—	—	20.47

pares predicted and experimental data from different references. In almost all cases, the predictions fall in the range of solubility parameters found in the literature. Some experimental results appear to be questionable. A solubility parameter of 15.76 MPa<sup>1/2</sup> for polyethylene is inconsistent with the trend displayed by *n*-alkanes. Indeed, *n*-tridecane has a solubility parameter of at least 16.00 MPa<sup>1/2</sup>. Since the solubility parameter increases with the molecular weight, a greater value is expected for polyethylene. The GCLF-EOS was found to have errors of less than 8% for most nonstrongly hydrogen-bonding pure solvents. An error of the same order is expected for polymeric systems. The predicted values can therefore be used as a basis for the choice of a solvent or a mixture of solvents. For strongly hydrogen-bonding systems, a higher error is expected. Still, even if this error was  $\pm 20\%$ , this range is less than the range of values found in the literature.

Oligomers are known to have different properties than those of the corresponding polymer. Figure 1 shows the evolution of the solubility parameters of *n*-alkanes with the number of carbons. This approach could be used for any polymer or plasticizer. Data of this type are rarely available.

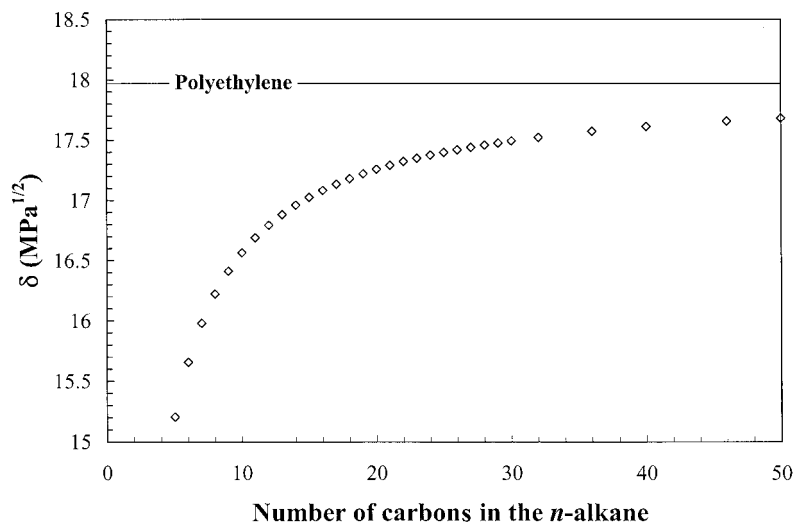
Most of the solubility parameters found in the literature are at 25°C. The EOS approach has the flexibility of providing data at any operating condition. Solubility parameters applicable to the supercritical region are almost not found in the lit-

erature. The solvent power of a supercritical fluid can be tuned by changing the operating conditions. Figure 2 shows the solubility parameter of carbon dioxide with pressure at 323.15 K. A pressure of 140 MPa is needed to reach a solubility parameter of 15 MPa<sup>1/2</sup>, which is lower than that of most common polymers. This result agrees with the experimental observation that supercritical CO<sub>2</sub> is often a bad solvent for polymers. It also explains why a pressure of 270 MPa is needed for the polyethylene synthesis.

The solvent power is generally associated with the solvent density. At 200 MPa and 50°C, the density of CO<sub>2</sub> is almost equal to 1 g/cm<sup>3</sup>. At this rather high density, the cohesive energy is not high enough to give carbon dioxide the solvent power to dissolve common polymers. Several articles reported the use of an organic cosolvent to increase the solvent power of CO<sub>2</sub>. Mixtures of liquid solvents are also often used to dissolve polymers.

### Mixtures

The calculation of the solubility parameter for mixtures requires the interaction parameter  $k_{12}$ , which is a correction to the geometric mean expression given in eq. (12). Lee and Danner<sup>16</sup> developed a group-contribution method for the estimation of this interaction parameter. Each pair of groups is characterized by an interaction parameter, which is correlated from binary liquid-vapor



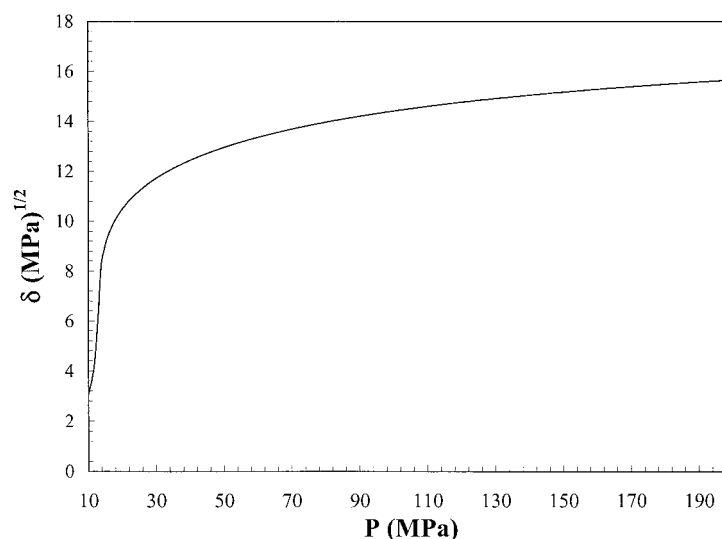
**Figure 1** Influence of the degree of polymerization of polyethylene on the solubility parameter at 298.15 K.

equilibrium. Table III lists the solubility parameters of some mixtures<sup>11</sup> and those predicted by the GCLG-EOS with a  $k_{12}$  estimated from the Lee and Danner group-contribution method and also a  $k_{12}$  equal to zero. The predictions of the GCLF-EOS are in very good agreement with the literature data for both cases. The interaction parameter does not seem to have a strong influence on the solubility parameter of liquid mixtures. The model can therefore be used even if the interaction parameters between the groups are not known. To gain better insight, the predictions

of the model are also compared against the solubility parameter of mixtures,  $\delta_m$ , obtained using<sup>11</sup>

$$\delta_m = \sum_i \phi_i \delta_i \quad (17)$$

where  $\delta_i$  and  $\phi_i$  are, respectively, the solubility parameter and volume fraction of component  $i$  in the mixture. The average error is only slightly higher than that of the model. The predictions are better for solvents of a similar chemical nature.



**Figure 2** Influence of pressure on the solubility parameter of supercritical carbon dioxide at 323.15 K.



**Table III Solubility Parameters of Mixtures at 298.15 K**

Mixtures (1/2)	$\phi_1$	$\delta$ (Ref. 11)	GCLF ( $k_{ij} \neq 0$ )	% Error	GCLF ( $k_{ij} = 0$ )	% Error	Eq. (18)	% Error
<i>n</i> -Heptane/diisobutyl ketone	0.5	15.6	15.75	0.98	15.79	1.24	15.98	2.40
<i>n</i> -Heptane/diisobutyl ketone	0.25	15.8	16.05	1.56	16.08	1.75	16.26	2.90
<i>n</i> -Heptane/ <i>n</i> -butyl acetate	0.667	16	16.07	0.44	16.10	0.63	16.16	1.02
<i>n</i> -Heptane/ <i>n</i> -butyl acetate	0.4	16.8	16.76	0.25	16.79	-0.07	16.37	-2.58
Cyclohexane/toluene	0.71	17.2	17.57	2.12	17.64	2.53	17.19	-0.05
Cyclohexane/toluene	0.4	17.6	18.02	2.38	18.10	2.84	17.65	0.31
Cyclohexane/benzene	0.5	17.8	17.89	0.49	17.97	0.94	17.73	-0.39
Diethyl ether/ <i>n</i> -butyl acetate	0.57	16.2	16.68	2.98	16.60	2.47	16.39	1.16
Diethyl ether/2-ethy-1-hexanol	0.667	16.6	16.79	1.15	17.05	2.73	17.13	3.18
Diethyl ether/2-ethy-1-hexanol	0.333	18	18.13	0.73	18.32	1.78	18.84	4.68
<i>n</i> -Butyl acetate/toluene	0.5	17.8	18.20	2.22	18.22	2.37	17.96	0.90
Dichloromethane/toluene	0.5	19	19.06	0.31	19.18	0.94	19.31	1.63
Average error				1.3		1.7		1.8

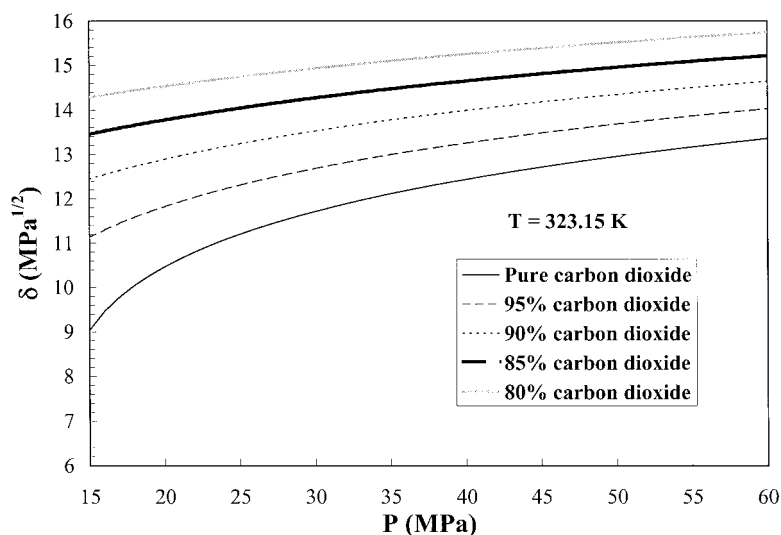
The data from ref. 10 are compared to the predictions of the GCLF-EOS for a  $k_{12}$  obtained by the group-contribution method of Lee and Danner, a  $k_{12}$  equal to zero, and the solubility parameter obtained from eq. (17).  $\phi_1$  is the volume fraction of component 1 in the mixture.

Since supercritical CO<sub>2</sub> is a poor solvent for polymers, a cosolvent is often added to enhance the solvent power. Figure 3 compares the solubility parameter of a propanol/carbon dioxide solution with the pressure and composition at 323.15 K. Propanol solutions have a significantly higher solubility parameter compared to that of pure carbon dioxide. A pressure of 140 MPa is required to reach a solubility parameter of 15 MPa<sup>1/2</sup> for pure CO<sub>2</sub>. This pressure constraint decreases to 53 and 32 MPa, respectively, for 85 and 80% CO<sub>2</sub>

solutions. In practice, the use of a cosolvent allows lower operating pressures and higher solubilities. This can be quite beneficial, for example, in the manufacture of foams.

## CONCLUSIONS

The solubility parameters of over 100 pure solvents were calculated from the GCLF-EOS using only the chemical structure as the input. The



**Figure 3** Influence of pressure and composition on the solubility parameter of carbon dioxide/propanol solutions at 323.15 K.

model gave satisfactory results for polar, nonpolar, and slightly hydrogen-bonding systems. A systematic overprediction of approximately 5–6% was found for alkanes and alkenes. This information could be used for practical engineering purposes. Molecular structures causing steric exclusion, however, were found to cause strong discrepancies in some cases.

The predictions for solvents involving strong hydrogen bonding is poor, particularly for short chains. As the molecular weight increases, a better agreement is obtained because of the decrease of the hydrogen-bonding contribution to the overall interactions. The GCLF–EOS consistently underestimates the solubility parameter of alcohols. For practical purposes, a good estimate is obtained by adding 8% to the predicted value.

The primary interest in the EOS approach to solubility parameters lies in its application to polymers and copolymers. The model is a good alternative to the different experimental methods that give large ranges of solubility parameters. For liquid solvents, large discrepancies should be expected for polymers involving hydrogen bonding. Moreover, the model does not take into account crystallinity, which may induce an additional source of error.

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