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The partial solubility parameters: An equation-of-state approach

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Abstract

The division of the well-known solubility parameter into its dispersion, polar, and hydrogen-bonding components has significantly upgraded its capacity and usefulness in the screening and selection of the appropriate solvents in Industry and in Laboratory. This work presents a new statistical thermodynamic approach for the estimation of these partial components over a broad range of temperature and pressure. Key to this approach is the development of explicit expressions for the contribution of dispersion, dipolar, and hydrogen-bonding interactions to the potential energy of the fluid. The approach is applicable to ordinary solvents, to supercritical fluids, as well as to high polymers. Information on various thermodynamic properties of fluids is used in order to estimate the three solubility parameter components. Extensive tables with the key parameters are presented. On the other hand, available information on these separate components is exploited in order to extract information for the thermodynamic behaviour of the fluids over an extended range of external conditions.

Keywords: Statistical thermodynamics; Cohesive energy density; Hansen solubility parameters; Solvent screening

1. Introduction

The solubility parameter, δ, originally introduced by Hildebrand and Scott [1], remains today one of the key parameters for selecting solvents in industry, characterizing surfaces, predicting solubility and degree of rubber swelling, polymer compatibility, chemical resistance, and permeation rates, and for numerous other applications. There is also much interest in utilizing solubility parameter for rationally designing new processes, such as the supercritical fluid, the coating, and the drug delivery processes [2–8].

One closely related concept to δ is the cohesive energy E, which is defined as the increase in the internal energy per mole of the system upon removal of all intermolecular interactions. When E is divided by the molar volume V, we obtain the cohesive energy density (ced), E/V, of the system. The solubility parameter is simply the square root of this cohesive energy density [1].

The conceptual simplicity of δ makes it most attractive in industry and in academia as well. Of course, the use of solubility parameter is not always successful and this very lack of total success stimulates continuing research. The central principle behind the use of δ is the historic alchemist maxim, "similia similibus solvuntur" ("like dissolves like"), probably, the oldest rule of solubility. This rule can, indeed, be a good guide in the study of solubility, as long as we can also define with sufficient precision the degree of likeness in the given system. This need for precision in the definition of likeness lead to the division of δ into its partial components or Hansen solubility parameters [5] δ_d, δ_p, and δ_{hb}, for the dispersion, the polar, and the hydrogen-bonding contribution, respectively. Thus, liquids with similar δ_d, δ_p, and δ_{hb}, are very likely to be miscible. The bulk of the developments in solubility parameter reside on this principle of "similarity matching" of properties. Since it is recognized, however, that a more appropriate principle would be the "complementary matching" of properties [9], the hydrogen-bonding component, δ_{hb}, is further subdivided into an acidic component, δ_a, and a basic component, δ_b, in order to account for the Lewis acid and Lewis base character of the substance [8–10].

Over the years the partial solubility parameters were determined for an enormous number of substances and lead to critical compilations available in the open literature [3,5]. This type of compilations is a most valuable source of information for the nature of the substances and their interactions with other substances.

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Starting from the original definition of cohesive energy density and solubility parameter, we have already proposed a systematic approach for estimating the latter over an extended range of temperature and pressure [11,12]. In this work it became clear that the hydrogen-bonding contribution could be calculated rather accurately from the hydrogen-bonding part of the potential energy E and the volume V of the system as obtained, for example, from the LFHB equation-of-state model [13]. The model, however, could not separate the dispersion and the polar components of the solubility parameters. The proposition was made to calculate δ_d from the solubility parameter of the corresponding homomorph hydrocarbon. Although this proposal could be valid for some classes of fluids, it could not be generalized.

In the present work we will extent our previous approach [11,12], in an effort to account for all three components of the solubility parameter. This will be done by cadopting the more recent and more accurate non-random hydrogen-bonding (NRHB) equation-of-state framework [14], which will be modified in order to explicitly account for dipole–dipole interactions and, thus, explicitly calculate the polar component, δ_p.

2. Theory

2.1. The equation-of-state framework

Let us consider a system of N molecules of a fluid at temperature T, external pressure P, and of volume V, which are assumed to be arranged on a quasi-lattice of coordination number z and of N_r sites, N_0 of which are empty. Each molecule is assumed to be divided in r segments of segmental volumes v^*, and to have $zq = zrs$ external contacts, s been its surface-to-volume ratio, a geometric characteristic of the molecule. The total number N_r of lattice sites is given by

$$N_r = rN + N_0 \tag{1}$$

Following our previous practice [14], we may write for the configurational partition function of the fluid in the N, P, and T ensemble and in its maximum term approximation:

$$\begin{aligned} Q(N, T, P) &= Q_\mathrm{R} Q_\mathrm{NR} Q_\mathrm{hb} \\ &= \Omega_\mathrm{R}\Omega_\mathrm{NR}\Omega_\mathrm{hb} \exp\frac{-E_\mathrm{d}}{kT} \exp\frac{-E_\mathrm{p}}{kT} \exp\frac{-E_\mathrm{hb}}{kT} \exp\frac{-PV}{kT} \end{aligned} \tag{2}$$

E_d, E_p, and E_hb in Eq. (2) are the dispersion, polar, and hydrogen-bonding components, respectively, of the potential energy of the system. The detailed rationale behind the form of the combinatorial term, Ω_R, and its correction factors for non-random distribution of free volume, Ω_NR, and for the hydrogen-bonding, Ω_hb, can be found in the previous work [14]. Here we will simply reproduce the final equations, namely:

$$\Omega_\mathrm{R} = \omega^N \frac{N_r! N_r^{lN}}{N_0! N!} \left(\frac{N_q!}{N_r!}\right)^{z/2} \tag{3}$$

where

$$l = \frac{z}{2}(r - q) - (r - 1) \tag{4}$$

while the total number of intermolecular contacts in the system is given by

$$zN_q = zqN + zN_0 \tag{5}$$

In Eq. (3), ω is a characteristic quantity for each fluid that takes into account the flexibility and the symmetry of the molecule and which cancels out in all applications of our interest.

In the followings we will need the site fractions f_0 and f for the empty sites and the molecular segments, respectively, which are related by

$$f_0 = \frac{N_0}{N_r} = \frac{N_r - rN}{N_r} = 1 - f \tag{6}$$

For the second factor, Ω_NR, we may use various expressions available in the open literature [14]. The most classical is Guggenheim's quasi-chemical expression [15]:

$$\Omega_\mathrm{NR} = \frac{N_{rr}^0! N_{00}^0! \left[\left(\frac{N_{r0}^0}{2}\right)!\right]^2}{N_{rr}! N_{00}! \left[\left(\frac{N_{r0}}{2}\right)!\right]^2} \tag{7}$$

where N_{rr} is the number of external contacts between the segments belonging to molecules, N_{00} is the number of contacts between the empty sites, and N_{r0} is the number of contacts between a molecular segment and an empty site. The superscript 0 refers to the case of randomly distributed empty sites. In this random case we have:

$$N_{rr}^0 = \frac{1}{2} zqN \frac{qN}{N_0 + qN} = \frac{z}{2} qN\theta_r \tag{8}$$

$$N_{00}^0 = \frac{1}{2} N_0 z \frac{N_0}{N_\mathrm{q}} = \frac{z}{2} N_0\theta_0 \tag{9}$$

and

$$N_{r0}^0 = zqN\frac{N_0}{N_q} = zN_0\frac{qN}{N_q} = zqN\theta_0 = zN_0\theta_r \tag{10}$$

where

$$\theta_r = 1 - \theta_0 = \frac{\frac{q}{r}}{\frac{q}{r} + \tilde{v} - 1} \tag{11}$$

and the reduced volume is defined as

$$\tilde{v} = \frac{V}{V^*} = \frac{rN\tilde{v}v^*}{rNv^*} = \frac{1}{\tilde{\rho}} \tag{12}$$

$\tilde{\rho}$ being the reduced density.

The corresponding number of intersegmental contacts N_{ij} in the non-random case are given by the following equations:

$$N_{rr} = N_{rr}^0\Gamma_{rr} = \frac{z}{2} qN\theta_r\Gamma_{rr}, \qquad N_{00} = N_{00}^0\Gamma_{00},$$

$$N_{r0} = N_{r0}^0\Gamma_{r0} \tag{13}$$