Solubility Parameters: A Versatile Concept

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The main objectives of this contribution are (I) providing a brief overview of the evolution of the *solubility parameter (δ_i) concept*, (II) presentation of the key physicochemical aspects of popular δ_i-related models in solution chemistry, and (III) a concise survey of a few selected applications in physical chemistry and chemical engineering [1]. Prediction of thermodynamic properties of liquid nonelectrolyte solutions from properties of the pure constituents has come a long way since the classic studies of *Scatchard* and *Hildebrand* [2,3] leading to *regular solution theory* for which δ_i is the pivotal property [4]:

$$\delta_i(T,P) \equiv \sqrt{-U_i^{\mathrm{r,L,*}}(T,P)/V_i^{\mathrm{L,*}}(T,P)},$$

where $U_i^{\mathrm{r,L,*}}$ denotes the molar residual internal energy of pure liquid component *i*, and $V_i^{\mathrm{L,*}}$ is its molar volume, *i.e.* δ_i is the square root of the *cohesive energy density*.

The frequently neglected temperature and pressure dependence of δ_i will be discussed, for instance *via* a generalized corresponding states theory approach:

$$\delta_i / P_{\mathrm{c},i}^{1/2} = \delta_{\mathrm{r},i}^{(0)}(T_{\mathrm{r},i}) + \omega_i \delta_{\mathrm{r},i}^{(1)}(T_{\mathrm{r},i}) + \omega_i^2 \delta_{\mathrm{r},i}^{(2)}(T_{\mathrm{r},i}),$$

$$\delta_{\mathrm{r},i}^{(p)}(T_{\mathrm{r},i}) = a^{(p)} + b^{(p)} T_{\mathrm{r},i} + c^{(p)} T_{\mathrm{r},i}^2 + d^{(p)} T_{\mathrm{r},i}^3,\ p = 0,\ 1 \text{ or } 2,$$

where all the symbols have their customary significance.

Finally, extensions to *multi-dimensional* solubility parameter models will be indicated [5], which quantities are used with mixtures containing strongly polar and/or hydrogen-bonded substances. The most widely used *three-dimensional* solubility parameter was introduced by *Hansen* in 1967 [6], and the *50th Anniversary HSP Conference* will take place at the University of York, UK, 5 – 7 April 2017.

[1] E. Wilhelm, *Solubility Parameters: A Brief Review*, in: *Enthalpy and Internal Energy: Liquids Solutions and Vapours*, E. Wilhelm and T. M. Letcher, eds., The Royal Society of Chemistry/IACT, Cambridge, UK, 2017.

[2] G. Scatchard, Chem. Rev. **8**, 321-333 (1931).

[3] J. H. Hildebrand and S. E. Wood, J. Chem. Phys. **1**, 817-822 (1933).

[4] J. H. Hildebrand and R. L. Scott, *The Solubility of Nonelectrolytes*, 3rd edn, Reinhold Publishing Corporation, New York, USA, 1950.

[5] A. F. M. Barton, *CRC Handbook of Solubility Parameters and other Cohesion Parameters*, CRC Press, Boca Raton, Florida, USA, 2nd edn, 1991.

[6] (a) C. M. Hansen, J. Paint. Techn. **39**, No. 505, 104-117 (1967); (b) C. M. Hansen, J. Paint. Techn. **39**, No. 511, 505-510 (1967); (c) C. M. Hansen and K. Skaarup, J. Paint. Techn. **39**, No. 511, 511-514 (1967).