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Review

Solubility Measurement Method and Mathematical Modeling in Supercritical Fluids

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Abstract. Supercritical fluids technology (SFT) is gaining significance application in the field of food and drug processing. Since supercritical fluid possess dual characteristic of gas and liquid, it exhibits outstanding extraction features such as high penetration ability and able to dissolve materials. To aid the design of processes including extraction, separation, purification, and synthesis, solubility data of compound of interest is required. In addition, with the solubility data, a more environmental friendly and productive operating condition can be resulted. However, there is lack of review that summarizes the method and correlation to gain this data. Thus, the review is accomplished to give concise discussion on the fundamental knowledge of solubility. This review will discuss the solubility measurement method, quantification method and mathematical correlation models for explaining the thermodynamic relationship of solubility.

Keywords: Supercritical fluid, Solubility measurement, quantification, mathematical correlation, semiempirical model, equation of state.

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1. Introduction

In recent years, the interest on applying supercritical fluid technology in various industries such as pharmaceutical [1-4] and food industries [5-7] is increasing. A supercritical fluid is a substance that its temperature and pressure is above the critical point, which liquid and gas phase can coexist. At this stage, liquid density becomes lesser due to thermal expansion while gas becomes denser due to rising of pressure. These two densities are converging and ultimately, at the critical point of fluid, densities of two phases become identical. At this point, both gas and liquid phases become indistinguishable as the interphase that made two phases clearly visible will be disappeared. Therefore, supercritical fluid is penetrable and able to dissolve materials, which offering both gaseous and liquid property.

A near critical region fluid is either an expanded liquid or highly compressed gas. Supercritical fluids exhibit a unique density-related property that its dissolving power is strongly dependent on pressure. At higher pressure, the dissolving power of the supercritical fluid is higher, thus a better solvent [8]. This unique property of supercritical fluid realizes many processes such as extraction [9-11], purification [12, 13], fractionation [13-16], crystallization [17] and particle design [18-23]. Other than these, there are still many advantages using supercritical fluid technology including less energy consumed, lower mass transfer resistance, high selectivity of supercritical fluid, clean and recyclable process, and easy to separate extracted materials by simply varying temperature and pressure. Supercritical fluid is also being used as solvent to initiate new reaction processes for hydrolysis or partial oxidation because of its excellent transportability and dissolving power, as well as good solubility control. For instance, Kobe Steel recycles Tolylene diisocyanate (TDI) by hydrolyzing it into process raw material Toluenediamine (TDA) in supercritical water and chemical recycling of polyethylene terephthalate (PET) containers [24]. Other than this, Wahyudiono et al. [25] also uses supercritical fluid technology to convert organic waste into useful chemical compound and oxidize harmful waste to an inoffensive and simpler form. This technology is useful because sub and supercritical condition of water treatment can promote oxidation, hydrolysis and dehydration reaction of organic waste. In supercritical state, properties of water such as density and dielectric constant can be easily controlled over different temperature and pressure to increase solubility of organic waste. In addition, in terms of protecting the environment and reducing industry impact on nature, transesterification reaction that produces biodiesel can become greener by replacing the conventional catalytic process with sub and supercritical process [26]. Biodiesel produced by non-catalytic reaction can reduce the problem of recovering and treating catalyst, reduce wastewater, decrease in processing cost and reaction time, and have simpler downstream purification procedures.

Of many supercritical fluids, carbon dioxide is widely chosen in many studies due to its outstanding features. Firstly, carbon dioxide has mild critical temperature and pressure (31.3 °C and 71.9 bar), thus it is easy and convenient to separate heat-liable substances. Carbon dioxide offers small and linear molecular structure which causes diffusivity activity faster than other conventional liquid solvents. Besides, due to this characteristic, it is a good solvent for solutes that are sensitive to extreme condition. Also, carbon dioxide is cheap compared to other fluids and high purity of carbon dioxide is easy obtainable, and it is non-toxic and non-flammable. In supercritical state, carbon dioxide behaves as hydrophobic solvent, thus it is miscible with various kinds of organic solvents and thus able to extract most nonpolar materials. Furthermore, supercritical carbon dioxide will not leave any solvent residue in the extract and thus will not pollute the extract or making the separation process even harder. Supercritical carbon dioxide is widely used to replace certain organic solvents and toxic freons for some sensitive application, for instance, food and pharmaceutical sectors.

For all the processes that utilized supercritical fluid technology, solubility data is the most crucial and handy thermodynamic parameter that required to design and scale up the system [1]. With the knowledge of solubility data, the process yield, rate, design and economy can be optimized. Also, solubility can affect the size, shape, surface structure and morphology of products [18, 27, 28]. For instance, the particle formation technology needs reliable and fast determination of solubility data that falls within the low range 10-9 to 10-4 mole fraction [29]. Therefore, before any practical supercritical fluid technology, solubility data of the particular solute in specific supercritical solvent is needed. In brief, for any technology dealing with supercritical fluid, the main concern is to evaluate the ability of fluid to dissolve a solute of processed. Generally, experiment determines the phase equilibria of solute in high pressure solvent. The experiment data obtained are correlated with intensive variables such as pressure, temperature and equilibrium compositions by models. For the case of multicomponent mixtures, or complex mixtures consisted of low volatile substances, more difficulties gained when carry out the phase equilibrium experiment due to more number of components involved, low vapor pressures and great differences in compound properties [30].

It is not necessary that high solubility of solute in certain solvent is a good option. Different process requires different magnitude of solubility; in supercritical extraction processes, high solubility is desired, while low solubility is prefer for carbon dioxide or organic solvent mixtures used in the process of supercritical anti-solvent precipitation to synthesis particles [31].

Although many solubility studies had done on different compounds, there is still lacking of reviews that summarize and discuss the common solubility measurement method, including the experimental running and quantification method to determine amount of solute solubilized in supercritical fluids. Also, a condensed form of model list that use to correlate solubility with thermodynamic data is also scarce. Thus, in this review paper, the mentioned affairs will be discussed and compared briefly.

2. Solubility Measurement Method

Solubility of solute in supercritical solvent is determined by measuring the amount of solute in the solution, giving the result in terms of mass fraction or mole fraction. In supercritical condition, the solute can archive a metastable equilibrium with the solvent. An addition of cosolvent or seed crystal can even create an influence to the system which will significantly bring up the solubility [8]. Generally, there are two main methods to determine the solubility of a compound, static and dynamic method. In static method, equilibrium state between the solute and the solvent is achieved before any sample is taken out to analyze the solubility. Static method carries out the equilibrium process in many ways which include recirculation of the solvent, agitation by magnetic stirrer, or simply trap the solvent in the equilibrium cell for some time. Three categories of static method can be concluded based on type of the vessel: analytic, synthetic and gravimetric.

In the case of static-analytic method, the vessel volume is constant, and the solute is contacted with a known volume of supercritical fluid. The sample of fluid is removed to determine the solubility of solute in the fluid. The key for static-analytical method is the sampling procedure as only a small volume of equilibrium solution should be drawn from the cell but deliver quantitatively to sample flask. This is to ensure that the cell is always remained at equilibrium state. However, this is very difficult to achieve in reality, thus some careful practices are taken to have approach that near to ideality. For instance, only remove small quantities by opening valves slowly and carefully, maintain the sample lines which include valves and sample flask clean and air tight, take average reading of few samples, take the samples with least effect on pressure drop [30]. In static-analytic approach, sample is drawn through a thin capillary as this can ensure only small quantity is taken out, then the sample is let to expand into a sample flask to separate as two phases: condensed and gaseous phase. The gaseous phase quantity is determined by measuring its volume or evaluating the pressure in a known expansion volume, while the condensed phase quantity is weighed or subjected to detailed analysis such as gas chromatography when multicomponent system involved.

Static-synthetic method is good in determining binary phase equilibria as well as phases encountered in multicomponent systems. In this method, the vessel temperature is controlled, and the volume can be changed by liquid mercury or movable piston inside the cell to adjust pressure for the experiment. Same as the static-analytical method, solute is mixed well with supercritical solvent, particularly stirrer. With this method, the operating condition is changed with known quantities and concentration of system components. Pressure is varied with constant temperature or temperature is varied with constant pressure so that a change of phase is detected. Therefore, in this method, the vessel is fit with sapphire window to visual detect the cloud point [32]. In most cases, pressure is varied as it is easier than to vary temperature, also it is more convenient to monitor volume and pressure change.

Static-gravimetric method involves keeping the solute in a small vial where it is subjected to pressure vessel that contains supercritical fluid. The vial is designed such that only the dissolved solute can permeate through the lid to the pressure vessel, but not the solute particles. This method is carried out in a way that known amount of solute is first placed in the vial, and pressure vessel is filled with supercritical fluid. The supercritical fluid dissolves the solute in the vial, and brings the dissolved material out from the vial. Eventually, equilibrium state is achieved. Then the vessel is depressurized, and the remaining solute is weighed gravimetrically.

On the other hand, in dynamic method, solute which is the condensed phase remains in equilibrium cell, while the supercritical fluid flows through the cell continuously. Supercritical fluid is contacted with the solute and achieved equilibrium during the residence time of supercritical fluid in the equilibrium cell. Then, the equilibrated solution is extracted and analyzed its equilibrium concentration. However, the supercritical fluid is not giving adequate time to fully contact with the solute and it is not mixed thoroughly with solute, the outlet flow can only be assumed to reach equilibrium. Operating conditions are carefully chosen so that the assumption can be more justifiable. This is the drawback of dynamic method, and recirculation of solvent flow can enhance the solubility equilibrium before discharge. Supercritical solvent is continuously flow through the equilibrium cell that filled with solute at low flow rate. Low flow rate of supercritical solvent allows the outlet stream to reach equilibrium due to sufficient retention time. Thus, before carrying out the experiment, optimization works should be done to find the best flow rate of supercritical fluid. A suitable flow rate can be determined via trial and error method at same operating conditions for the experiment until a fixed and constant value of solubility is obtained.

Both static and dynamic methods have their benefits as well as shortcomings. Static method although is rather simple and high direct applicability, it is more expensive, slower and more prone to inaccuracies that caused by leaks arose from large quantities of valves and fittings. The result from static method is very much dependent on skill of sampling, and the expertise. Also, errors may occur from multiple samplings, especially when data at multiple pressure and temperature are collected from a single solute or solvent loading. Another disadvantage that using static method is removing a small amount of equilibrated fluid phase from the equilibrium cell may cause pressure drop or change in temperature, thus disturbs the equilibrium phase significantly, which solute may be lost by precipitation in the valves or sampling lines in static method due to volume change [31]. Besides, this can also cause changes in composition of the equilibrated solution and inadequate separation of phases, which eventually causing it has limitations in critical region. Furthermore, this method is not applicable for low equilibrium concentration of solute. As for the case of static-synthetic method, pressure is changed until phase change is detected by vision. This means that equilibrium pressure cannot be determined accurately. Static-gravimetric method, on the other hand, only effective for solute that presents mole fraction solubility greater than 10-3. Other limitations do apply for static-gravimetric method such as the solid should not melt under experimental conditions, and absorb negligible amount of supercritical fluid.

Dynamic method has several advantages such as sampling procedure is easy, faster process, large amount of solubility data can be obtained fast, the apparatus can be assembled easily from available parts, fractionation data can be obtained other than just equilibrium data, and carbon dioxide flow measurement can be done with a simple gas flow meter at the exit [31]. However, in dynamic method, mass transfer rate between the supercritical solvent and solute may be an issue as the solute concentration may not reach its equilibrium value. Thus, sufficient solute is needed to saturate the supercritical solvent that flows enough slow. The solute amount is predicted by referring the available solubility value of other compounds with similar characteristic. In brief, there is no one best method as it is chosen according different problem. Static-analytical method is suitable for multicomponent systems with low volatile compounds; however it is not appropriate for systems in critical region. Dynamic method is applicable for determining the solubility of low volatile compound in supercritical fluid, even though the compound has very low solubilities. On the other hand, static-synthetic method is more useful on measuring the phase equilibrium and screening for phase region.

3. Quantification Method

After the equilibrium process, quantification of sample plays important role as well to determine the amount of solute in the supercritical solvent accurately. Similarly, there are two main methods, off-line and on-line quantification. In the off-line method, a small volume of sample is removed by solvent trap, and then analyzed by various chemical analyses such as gravimetric method, UV-spectrophotometry, High Performance Liquid Chromatography, Gas chromatography and dielectric constant techniques. In the solvent trap, the amount of solvent, kind of solvent and cooling temperature of the solvent will result diverse solute removal efficiency [33]. Off-line measurements take more time and require additional processing step such as dilution, concentration or change of solvent type which can lead to errors [29].

As for the on-line sampling, chemical analyses system is direct connected to the sample loop, allowing response from the outlet stream direct analyzed by computer software. Compared to off-line sampling, on-line sampling is a more effective, reliable and fast quantification technique. However, it has several drawbacks such as calibration of the on-line response and adjustment of chromatography condition are difficult and take long time, and detector can lead to errors because of the potential saturation of the sensor by high solubility compound [34]. Also, if complicated compound is encountered, on-line analysis may not be useful as the response will be chaotic. Although the on-line analysis has more advantages over an off-line method, if static method is used, on-line analysis is not recommended because reduction of analysis time is not significant comparing the total time taken for the system to equilibrate in static method. Furthermore, the presence of carbon dioxide gas in the mobile phase makes the analysis more complicated [29].

4. Mathematical Correlation Models

Mathematical models are used to correlate the solubility data in order to determine the equilibrium solubility of solute in a supercritical fluid at different condition. This is because determination of solid solubility in every different point of temperature and pressure experimentally is difficult and not possible.

4.1. Empirical Fit

The most straight-forward and easiest way of correlating data is empirical fit, where relationship of solubility data to thermodynamic property, say pressure or density, is fitted directly, either linearly or other best-represented form. Li et al. [35] fitted solubility data of 2-naphthol and anthracene to pressure and density in form of curvilinear while linear fit model can be seen in Hybertson [36] work, in which sesquiterpene alcohol patchoulol is dealt. On the other hand, other more accurate and sophisticated models can also be used to predict the solubility behavior of solute, generally there are three types of models, namely solubility parameter model or solution model, density based semiempirical model and chemical association based semiempirical model [37].

4.2. Solubility Parameter Model

Solubility parameter model uses some solubility parameters and information of heat of fusion, sublimation pressure of solute, melting temperature, critical temperature, critical pressure, acentric factor and molar volume of solute and supercritical fluid to predict equilibrium solubility. In this model, supercritical fluid is treated as expanded liquid rather than gas [27]. Through this model, a lot of information is taken from literature or estimated by various assumptions and equation of states, therefore its accuracy is relatively lower than semiempirical model. Another drawback of this model is that solute properties are normally not available for complex structural compounds, in which complicated computational prediction and group contribution method need to involve [38]. Some common used equation of states that aid the modeling of solubility parameter model are Soave-Redlich-Kwong equation of state, Peng-Robinson equation of state, Yu-Lu-Iwai equation of state, Lee-Kesler-Plocker equation of state and Mohsen-Nia-Moddaress-Mansoori equation of state. Comparatively, these equations of state are more complicated than empirical or semiempirical model, because it requires more efforts to figure out the unknown constant in the model. Some solubility parameter models were listed in Table 1.

4.3. Semiempirical Model

As semi-empirical model is derived from some extent of experiments or observations, it is rather accurate and explainable than the model that solely relying on theoretical basis. However, one disadvantage of this model is solubility data is needed for correlation purpose [38]. Also, this model is a more realistic and practical approach as it can be applied to multicomponent systems with unknown components [30]. Accuracy of models is tested by many least error methods such as absolute average relative deviation (AARD) or the error sum of squares (SSE). Some common semiempirical models are Chrastil model, Mendez-Santiago and Teja model, Kumar and Johnston model, Sung & Shim model, Bartle model, Adachi and Lu model, Gordillo model and etc. which were shown in details in Table 2.

Table 1. Equation of State based models.

Model	Equation		Example of compound
Solution Model [39, 40]	$\ln \mathrm{y}_2 = \frac{\Delta_f H}{RT}\left(\frac{T}{T_2{}^m} - 1\right) - \frac{v_2}{RT}(\delta_2 - \delta_1)^2$	(1)	Benzene derivatives [37], Noble-metal-chelates [41]
Solution Model coupled with Flory-Huggins Equation [42]	$\ln y_2 = \frac{\Delta_f H}{RT}\left(\frac{T}{T_2{}^m} - 1\right) - \frac{v_2}{RT}(\delta_2 - \delta_1)^2 - 1 + \frac{v_2}{v_1} - \ln\frac{v_2}{v_1}$	(2)	Copper compound [43], pharmaceutical compound [27]
Soave-Redlich-Kwong Equation of State [44]	$P = \frac{RT}{v-b} - \frac{a_{cr}\alpha}{v(v+b)}$	(3)	Napthalene and phenanthrene [45]
Peng-Robinson Equation of State [46]	$P = \frac{RT}{v-b} - \frac{a_{cr}\alpha}{v(v+b)+b(v-b)}$	(4)	Methyl anthranilate [47], dodecanoic and tetradecanoic acid [48]
Yu-Lu-Iwai Equation of State [49]	$P = \frac{RT}{v-b} - \frac{a_{cr}\alpha}{v(v+c)+b(3v+c)}$	(5)	Napthalene and phenanthrene [45]
Lee Kesler Plocker Equation of State [50]	$z = z^o + \frac{\omega}{\omega^r}(z^r - z^o)$	(6)	β-carotene and nimodipine [51]
Mohsen-Nia-Moddaress-Mansoori [52, 53]	$P = \frac{RT(v+1.3191b)}{v(v-b)} - \frac{a_{cr}\alpha}{v(v+c)}$	(7)	Cholesterol and nimbin [51]

4.3.1. Density Based Semiempirical Model

Density based semiempirical models were developed from theory of dilute solutions. This theory involves expansion of Helmholtz energy around the solvent critical point in order to describe properties of infinite dilute solutions. Simplified Henry's law constants and infinite dilution partition coefficients expressions can be obtained by eliminating higher order terms in the expansion of Helmholtz energy [54]. Some examples of density based semiempirical models are Mendez-santiago Teja model, Bartle model, Sung and Shim model, Kumar and Johnston model, Adachi and Lu model, Yu model, and Gordillo model. As different models fit different case of solute solvent selection and thermodynamic condition, some researchers have modified these models to obtain a much better correlation [55]. Table 2 summarized some common semiempirical models used in correlating solubility with thermodynamic variables. The constants in the equation are coefficients that estimated by regressions of experimental data. Although many semi-empirical models available, there is no one universal model that best fit sets of solubility data from different cases and studies. Therefore, trial and error and comparison effort are needed to find the best correlation model that fit the experiment data.

Table 2. Common used semi-empirical models.

Model	Equation		Example of compound
Mendez-santiago-Teja [54]	$T\ln\frac{y_2P}{P_2^{sub}} = A + B\rho_1$	(8)	Cetirizine [56], Ibuprofen [55]
Modified Mendez-santiago-Teja [54]	$T\ln y_2P = A + B\rho_1 + CT$	(9)	Ibuprofen [55]
Bartle [57]	$\ln\frac{y_2P}{P_{ref}} = A + B\rho_2$	(10)	Cetirizine [56], Ibuprofen [55]
Modified Bartle [57]	$\ln\frac{y_2P}{P_{ref}} = A + \frac{B}{T} + C(\rho_2 - \rho_{ref})$	(11)	Ibuprofen [55], Statin drug [1]
Sung and Shim [58]	$\ln y_2 = A + \frac{B}{T} + \left(C + \frac{D}{T}\right)\ln\rho_1$	(12)	Ibuprofen [55]
Kumar and Johnston [59]	$\ln y_2 = A + B\rho_1 + \frac{C}{T}$	(13)	Cetirizine [56], Ibuprofen [55]
Adachi and Lu [60]	$c_2 = \rho_2^{\left(A + B\rho_2 + C\rho_2^2\right)}\exp\left(\frac{a_1}{T} + b_1\right)$	(14)	Triphenylmethane [32]
Yu [61]	$y_2 = A + BP + CP^2 + DPT(1 - y_2) + ET + FT^2$	(15)	Fatty acid, fatty acid esters, triglycerides, fats and oils [61]
Gordillo [62]	$\ln y_2 = A + BP + CP^2 + DPT_1 + ET_1 + FT_1^2$	(16)	Benzene derivative [37]
Chrastil [63]	$\ln c_2 = A + \frac{B}{T} + C\ln\rho_2$	(17)	Napthol isomers [64], Methyl anthranilate [47], Flurbiprofen [65], Metal acetylacetonate [66]
Del Valle and Aguilera [67]	$\ln c_2 = A + B\ln\rho + \frac{C}{T} + \frac{D}{T^2}$	(18)	Vegetable oils [67]
Tan [68]	$\ln y_2 = A\ln\rho_2T + b\rho_2 + \frac{C}{T} + D$	(19)	Artemisinin [69], Troeger's Base [70]

4.3.2. Chemical Association Based Semiempirical Model

Association theory is used to develop chemical association based semiempirical model, where fugacity calculation involves the solvate complex (AB_k). The solvate complex is a cluster that formed by a molecule of solute A associated with several (k) molecules of solvent B [71]. The solvent molecules, solute molecules and solvent-solute clusters are then in equilibrium with supercritical fluid system. Law of mass action is then used to calculate the equilibrium concentration [63].

Chrastil model was developed based on chemical association law and it is one of the most popular semiemipirical model used currently since there has a good promise with experimental data over wide range of temperature and pressure [63]. Del Valle's model modified Chrastil model with addition of second order temperature term for wider temperature range and solute's solubility under 100 g/L [67]. Tan's model combined both physical interaction and association effects of molecules to cater the error resulted from small density in near critical region [68, 72]. In comparison to other chemical association based models that used to correlate solubility with either density or temperature and pressure, Rajasekhar [71] has developed a new chemical association based semiempirical model that involves four parameters in the equation. Rajasekhar's model is formed based on the association of interest solute with the supercritical fluid and correlates solubility with temperature, pressure, and density. As this model considers four parameters in correlating the solubility, and together with the association number of solute (k) in supercritical fluid, it has been reported that this model is generally more accurate than other existing models for drug case [37]. The developed chemical association model was shown:

$$y_2 = \left(\frac{P}{P_2^{sub}} \right)^{(k-1)} \exp\left(\frac{A}{T} + B\rho_1 + C \right) \tag{20}$$

Similar to other common semiempirical models as discussed earlier, the constants in the equation (20) are determined by regression method; while the density is calculated from Span and Wagner equation of state [73]. This model is an alternative to existing semiempirical models because it offers better accuracy especially to cases that drug solubility are studied, and it is superior to equation of states as it involves less parameters that are difficult to obtain or not available. Example of solutes suitable with this model are antipyrine, aspirin, benzoin, acetanilide, cholesterol, flurbiprofen and other common pharmaceutical compounds that contained steroids, antioxidants, statins, antibiotics and anti-inflammatory.

5. Conclusion

Supercritical fluid technology offers wide variety of advantages in industrial physical processes. Therefore, researchers raised their interest and study more about the supercritical fluid technology in recent years, to eventually replace the organic fluid used in conventional processes which is environmentally and economically infeasible. However, different types of supercritical fluid present different range of solubility value on many kinds of solutes. In other words, solubility data is subjective to specific solvent and solute. In order to realize the industrial physical processes, solubility data plays an important role because processes can be optimized by modifying the process working condition. Solubility data can be developed by static or dynamic experimental method, followed by different type of quantification methods and then mathematical modeling for prediction and scale up. Fitting the experimental solubility data with a mathematical model is tedious, especially involving equation of states. Thus, further advances are needed to develop a common model to fit different categories of solute.

Nomenclature

y_2	Solubility (Mole fraction)
c_2	Solubility (g L-1)
T	Absolute temperature (K)
T_1	Temperature (oC)
ρ_1	Molar density of fluid (mol L-1 or mol mL-1)
ρ_2	Density (g L-1)
ρ	Density (g mL-1)
ρ_{ref}	Reference density (700 g L-1)
P	Pressure (bar)
P_{ref}	Reference Pressure (1 bar)
P_2^{sub}	Sublimation pressure (bar)
a_{cr}	Attraction parameter at critical temperature
α	Dimensionless function of reduce temperature and acentric factor, unity at critical temperature
b	van der Waals covolume
c	Equation of state parameter

a_1	Constant depending on enthalpy of solvatation
b_1	Constant depending on molar mass of solvent and solute
k	Association number of solute
R	Gas constant (J mol-1 K-1)
$\Delta_f H$	Heat of fusion (J mol-1)
T_2^m	Melting temperature of solute (K)
δ_1	Solubility constant of supercritical fluid (J1/2 m-3/2 or MPa1/2)
δ_2	Solubility constant of solute (J1/2 m-3/2 or MPa1/2)
v	Molar volume (m3 mol-1 or dm3 mol-1)
v_1	Molar volume of supercritical fluid (m3 mol-1 or dm3 mol-1)
v_2	Molar volume of solute (m3 mol-1 or dm3 mol-1)
z	Compressibility factor
z^o	Compressibility factor at standard state
z^r	Compressibility factor of reference fluid
ω	Acentric factor
ω^r	Acentric factor of reference fluid
A, B, C, D, E, F	Adjustable parameter

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