Korean J. Chem. Eng., **22**(3), 452-456 (2005)

Prediction of the Infinite-dilution Partial Molar Volumes of Organic Solutes in Supercritical Carbon Dioxide Using the Kirkwood-Buff Fluctuation Integral with the Hard Sphere Expansion (HSE) Theory

Yong Jung Kwon† **and Won Gyu Lee**

Department of Chemical Engineering, Kangwon National University, Kangwon-do 200-701, Republic of Korea

(*Received 27 September 2004 • accepted 14 February 2005*)

Abstract−Two thermodynamic models were used to predict the infinite dilution partial molar volumes (PMVs) of organic solutes in supercritical carbon dioxide: (1) the Kirkwood Buff fluctuation integral with the hard sphere expansion (HSE) theory incorporated (KB-HSE fluctuation integral method) and (2) the Peng-Robinson equation of state with the classical mixing rule. While an equation of state only for pure supercritical carbon dioxide is needed in the KB-HSE fluctuation integral model, and thus, there is no need to know the critical properties of solutes, two molecular parameters (one size parameter σ_{12} and one dimensionless parameter α_{12}) in the KB-HSE fluctuation integral model are determined to fit the experimental data published on the infinite dilution PMVs of solutes. The KB-HSE fluctuation integral method produced better results on the infinite dilution PMVs of eight organic solutes tested in this work than the Peng-Robinson equation of state with the classical mixing rule.

Key words: Partial Molar Volumes, Supercritical Fluid, Hard Sphere Expansion

INTRODUCTION

Over the last few decades, supercritical fluids with gas-like and liquid-like characteristics have received much attention due to their unique advantages and potential applications in industry. Supercritical fluids have high solvent strength which leads to the development of supercritical fluid extraction.

In SFE, the yield and selectivity are often extremely sensitive to pressure. Among the various properties of supercritical fluids, the infinite dilution partial molar volume (PMV) of a solute in supercritical fluids, $\overline{V}_2^\infty$, is very important in both theoretical and practical aspects because the data reflects the interactions between the solute and the supercritical solvent. The values of PMV give the pressure dependence of the solubility or fugacity coefficient ϕ_2^∞ of a solute in supercritical fluids [Prausnitz et al., 1986], which is used to calculate the solubility of liquids or solids in supercritical fluids.

Since the PMV is a differential quantity that describes the behavior of the supercritical fluid phase with a varying system pressure, it is useful for the development and testing of thermodynamic models proposed. There have been several approaches to calculate the infinite dilution PMVs of solutes in supercritical fluids. However, those can be mainly classified into two categories: 1) to use an equation of state with an appropriate mixing rule for supercritical fluid mixtures [Bader and Gasem, 1996: Coutsikos et al., 1997], and 2) to utilize statistical mechanics to provide better description of the infinite dilution PMVs of solids in supercritical fluids. Most of the second approaches can be summarized into making use of detailed expressions for the intermolecular potential energy and radial distribution function along with rigorous statistical-mechanical theories of mixtures [Liu and Macedo, 1995].

In the method to use an equation of state with appropriate mixing rules, information is needed on critical properties and acentric factor of solute. However, it is known to be very difficult to measure critical properties in many cases because of decomposition before the critical point is reached. For those components, estimation methods may be used, but those have not been known to be accurate [Schmitt et al., 1986].

One method in the second category is based on the Kirkwood-Buff solution theory [1951], which gives expression of the infinite dilution PMVs in terms of concentration fluctuations from the grand canonical ensemble. The hard-sphere expansion (HSE) theory [Mansoori and Leland, 1972], where the mean density approximation (MDA) is embedded and has been used to form a basis on the conformal solution method of mixtures [Kwon et al., 1997; Shin et al., 1998], will be used in this work to represent the solvent-solute fluctuation integral along with the Peng-Robinson equation of state [Peng and Robinson, 1976] only for supercritical fluid solvent.

The predicted results on the infinite dilution PMVs by the Kirkwood-Buff fluctuation integral along with the HSE theory (KB-HSE fluctuation integral model) in this work will be compared to those by the Peng-Robinson equation of state with the classical mixing rule for supercritical fluid mixtures.

THEORY

The partial molar volume (PMV), $\overline{V}_i$, is defined as:

$$\overline{V}_i = \left(\frac{\partial nV}{\partial n_i}\right)_{T,P,n_{j\neq i}} \tag{1}$$

where V is the molar volume and n is the total number of moles in mixture.

The infinite dilution PMV in a supercritical fluid mixture is a differential quantity obtained by taking the compositional derivative

---

[†] To whom correspondence should be addressed.

E-mail: yjkwon@kangwon.ac.kr

of the volume data for supercritical fluid-solute mixtures, which describes the behavior of the supercritical fluid phase with the varying system pressure, and is therefore useful for the development and testing of thermodynamic models proposed [Brennecke and Eckert, 1989].

The partial molar volume of a solute in a supercritical fluid can be calculated from the following standard thermodynamic relation:

$$\overline{V}_2^{\infty} = V_1 + \left(\frac{\partial V}{\partial n_2}\right)^{\infty}_{T,P,n_1} \quad \text{or} \quad \overline{V}_2^{\infty} = V_1 - \left(\frac{\partial V}{\partial y_1}\right)^{\infty}_{T,P_1} \tag{2}$$

where the superscript ∞ denotes infinite dilution of the solute in supercritical fluid, and the subscripts 1 and 2 refer to supercritical solvent fluid and diluted solute, respectively. Furthermore, the infinite dilution PMV from a standard pressure-explicit equation of state can be represented as follows [Debenedetti, 1987]:

$$\overline{V}_2^{\infty} = V_1 \kappa_{T_1} n_1 \left(\frac{\partial P}{\partial n_2}\right)^{\infty}_{T,nv,n_1}, \quad \kappa_{T_1} = -\frac{1}{V_1}\left(\frac{\partial V_1}{\partial P}\right)_T \tag{3}$$

where κ_{T_1} is the isothermal compressibility of the pure supercritical solvent fluid.

Near the critical point of the solvent, the following relation becomes effective:

$$\lim_{T,\rho \to critical} n_1 \left(\frac{\partial P}{\partial n_2}\right)^{\infty}_{T,V,n_1} = \left(\frac{\partial P}{\partial x_2}\right)^{\infty}_{T_c,\rho_c} \tag{4}$$

In Eq. (4), the isothermal, isobaric derivative of pressure with respect to composition, $(\partial P/\partial x_2)^{\infty}_{T_c,\rho_c}$, plays an important role in the thermodynamics of binary mixtures. The derivative becomes particularly important in dilute mixtures near the vapor-liquid critical point of the solvent. The value of the derivative in infinite dilution of the solute 2 and at the critical point of the solvent 1 has been called the 'Krichevskii' parameter [Levelt Sengers, 1991].

From Eqs. (3) and (4), the infinite dilution PMV can be expressed in the following form:

$$\overline{V}_2^{\infty} = V_1 \kappa_{T_1} \left(\frac{\partial P}{\partial x_2}\right)^{\infty}_{T_c,\rho_c} \tag{5}$$

In this work, two different methods to calculate the infinite dilution PMV of a solute in supercritical carbon dioxide by using Eq. (5) will be employed: (1) Kirkwood-Buff solution theory combined with the HSE method (KB-HSE fluctuation integral model) and (2) Peng-Robinson equation of state with the classical mixing rule.

1. Kirkwood-Buff Solution Theory

The Krichevskii parameter in Eq. (5) can be represented by the total correlation function integrals as follows [Chialvo, 1993]:

$$\left(\frac{\partial P}{\partial x_2}\right)^{\infty}_{T_c,\rho_c} = \rho k T (C_{11}^{o} - C_{12}^{\infty}) \tag{6}$$

where C_{11}^{o} and C_{12}^{∞} are the total correlation function integrals (TCFIs) of solvent-solvent in pure solvent and solvent-solute in infinite dilute solution, respectively.

Using the relation between TCFIs and fluctuation integrals [Ben-Naim, 1977], the Krichevskii parameter can be given by:

$$\left(\frac{\partial P}{\partial x_2}\right)^{\infty}_{T_c,\rho_c} = \frac{\rho^2 k T (G_{11}^{o} - G_{12}^{\infty})}{1 + \rho G_{11}^{o}} \tag{7}$$

Therefore, the infinite dilution partial molar volume of solute can be expressed as follows:

$$\overline{V}_2^{\infty} = V_1 \kappa_{T_1} \frac{\rho^2 k T (G_{11}^{o} - G_{12}^{\infty})}{1 + \rho_{11}^{o}} \tag{8}$$

where the subscript o refers to pure supercritical solvent. In this work, the Kirkwood-Buff solution theory [Kirkwood and Buff, 1951] is used to evaluate G_{11}^{o} and G_{12}^{∞} in Eq. (8). The Kirkwood-Buff solution theory provides the relation between thermodynamic properties (isothermal compressibility, partial molar volume, and derivative of chemical potential with respect to number of particle) and the integrals of the radial distribution function, G_{ij}, defined by

$$G_{ij} = \int_0^{\infty} [g_{ij}(r) - 1] 4\pi r^2 dr \tag{9}$$

where $g_{ij}(r)$ is the radial distribution function.

Cochran et al. [1987] developed the excluded-volume and local-composition (LC) models based on the Kirkwood-Buff fluctuation integrals to predict solubilities of organic solids in supercritical fluids; and Kwon and Mansoori [1993] successfully incorporated the fluctuation integrals into the HSE to give better results on solubility than former two models.

The MDA along with the HSE, developed by Mansoori and Leland [1972], provides a simple way to predict the radial distribution function of mixtures from the pure-fluid information and may be used to form a basis to give the relationship between G_{21} and G_{11}. The result is given by [Kwon and Mansoori, 1993]:

$$G_{21}^{\infty} = G_{12}^{\infty} = \alpha_{12} G_{11}^{o} + \frac{\sigma_{12}^3}{\sigma_{11}^3}\left(1 - \frac{\varepsilon_{12}}{\varepsilon_{11}}\right) G^{hs,o} \tag{10}$$

where the parameter α_{12} and $G^{hs,o}$ are expressed as follows:

$$\alpha_{12} = \frac{\sigma_{12}^3 \varepsilon_{12}}{\sigma_{11}^3 \varepsilon_{11}}, \quad G^{hs,o} = \sigma_{11}^3 \int_0^{\infty} [g^{hs}(y) - 1] 4\pi y^2 dy \tag{11}$$

In Eqs. (10) and (11), the superscript hs denotes hard sphere reference fluid, and σ and ε refer to size and energy parameter, respectively. From Eqs. (10) and (11), it is known that the fluctuation integral of solvent-solute, G_{21}^{∞}, can be represented by those of solvent-solvent, G_{11}^{o}, and pure hard-sphere reference fluid, $G^{hs,o}$.

The solvent-solvent fluctuation integral G_{11}^{o}, therefore, can be calculated from the PVT relation of pure component with an equation of state chosen:

$$G_{11}^{o} = \frac{1}{\rho^{o}}(\rho^{o} R T \kappa_T^{o} - 1) = \frac{1}{\rho^{o}}\left\{\left[Z^{o} + \rho^{o}\left(\frac{\partial Z^{o}}{\partial \rho^{o}}\right)\right]^{-1} - 1\right\} \tag{12}$$

For $G^{hs,o}$ in Eq. (10) to be evaluated, on the other hand, a simple hard sphere equation of state by Kim et al. [1986] is used in this work because of its simplicity and accuracy as in Kwon and Mansoori [1993].

It is shown from Eq. (10) that the fluctuation integral G_{12}^{∞} to represent solute-solvent interaction is expressed in terms of G_{11}^{o}, which accounts for solvent-solvent fluctuation integral and can be evaluated through Eq. (12). Whereas an equation of state only for pure supercritical solvent needs to be evaluated, and thus there is no need to know the critical properties of solute, it can be shown from Eq. (10) that three molecular parameters (two molecular size parameters σ_{11} and σ_{12}, and one dimensionless parameter α_{12} in this method are determined to fit experimental partial molar volume data.

2. Peng-Robinson Equation of State with a Mixing Rule

The Peng-Robinson equation of state [1976] is used in this work for a cubic equation of state to provide thermodynamic properties for pure supercritical fluid or mixtures. The Peng-Robinson equation of state is given by:

$$P=\frac{RT}{V-b}-\frac{a}{V^2+2bV-b^2} \tag{13}$$

where

$$a(T)=a_c\alpha(T)$$
$$a_c=\frac{0.45724R^2T_c^2}{P_c}$$
$$\alpha(T)=[1+F(\omega)(1-T_r^{0.5})]^2$$
$$F(\omega)=0.37464+1.54226\omega-0.26992\omega^2$$
$$b=\frac{0.07780RT_c}{P_c}$$

Since the classical mixing rule was originally proposed by van der Waals, various mixing rules have been developed. The following classical mixing rule is employed in the Peng-Robinson equation of state in this work:

$$a=\sum_i\sum_j(1-k_{ij})x_ix_i(a_ia_j)^{1/2}$$
$$b=\sum_i x_ib_i \tag{14}$$

where k_{ij} is the binary interaction parameter determined to adjust experimental data.

While the critical parameters (T_c, P_c) and acentric factor for the solute as well as for supercritical fluid component should be known to calculate the PMVs using the Peng-Robinson equation of state with the classical mixing rule, the critical parameters only for the pure supercritical fluid are needed in this work. Instead, the three molecular parameters are needed in the fluctuation method as mentioned above.

RESULTS AND DISCUSSION

To apply the KB-HSE fluctuation integral model to predict the infinite dilution PMVs and to compare the results with the Peng-Robinson equation of state with the classical mixing rule, eight aromatic compounds in supercritical carbon dioxide were tested. For evaluation of the solvent-solvent fluctuation integral G_{11}^o in Eq. (12) in the KB-HSE fluctuation integral model, the Peng-Robinson equation of state for pure supercritical carbon dioxide is also used.

The parameters to be determined in this work are σ_{11}, σ_{12}, and α_{12} in Eq. (10), as explained before. The value of the parameter σ_{11} in Eq. (10), which is the size parameter of supercritical fluid solvent, is fixed at 4.6 Å as in the work on the solubility prediction of solutes in supercritical fluids [Kwon and Mansoori, 1993] to reduce the number of adjustable parameters. The remaining two parameters were optimized to fit the experimental data on infinite dilution PMVs by using the following two object functions:

$$\text{obj}\,f_1=\sum_i^N\left(\frac{\bar{V}_i^{cal}-\bar{V}_i^{exp}}{\bar{V}_i^{exp}}\right)^2$$
$$\text{obif}_2=\sum_i^N(\bar{V}_i^{cal}-\bar{V}_i^{exp})^2 \tag{15}$$

Table 1. Pure compound data

Compound	T (K)	P (MPa)	ω	Data source
Carbon dioxide	304.2	7.374	0.225	Reid et al. [1987]
Naphthalene	748.4	4.052	0.302	Reid et al. [1987]
Phenanthrene	873.0	3.24	0.517	Bartle et al. [1987]
Fluorene	618.0	3.081	0.508	Reid et al. [1987]
DHA ethyl ester	867.1	1.102	0.860	Bharath et al. [1989]
DHA methyl ester	852.4	1.035	0.851	Liong et al. [1991]
EPA methyl ester	823.4	1.134	0.824	Liong et al. [1991]
Biphenyl	789.0	3.850	0.364	Reid et al. [1987]
Acenaphthylene[a]	-	-	-	-

[a]Not available

where N is the number of experimental points considered in this work.

While the size-related parameter σ_{12} is considered temperature independent, the dimensionless parameter α_{12}, which is related to the interaction energy parameter ε_{12} as shown in Eq. (11), can be considered to depend on temperature. In the method to use the Peng-Robinson equation of state with the classical mixing rule, the binary interaction parameter k_{12} in Eq. (14) is also regarded as temperature-dependent for better prediction of thermodynamics properties.

Table 1 lists the critical properties and acentric factor for carbon dioxide and solutes of interest in this work needed to calculate PMVs by the Peng-Robinson EOS with the classical mixing rule if those are available. The KB-HSE fluctuation integral model, however, does not require those properties for solutes but only for supercritical carbon dioxide as explained above.

Fig. 1 shows the prediction results on the infinite dilution PMVs of naphthalene in supercritical carbon dioxide by two methods considered in this work. While the values of σ_{12} and α_{12} in the KB-HSE fluctuation integral model were 7.27 Å and 4.68 Å, respectively, by fitting the experimental data published [Eckert et al., 1986], k_{12} in the Peng-Robinson equation of state was found to be 0.121. As shown in Fig. 1, the average absolute deviation (AAD) error by the

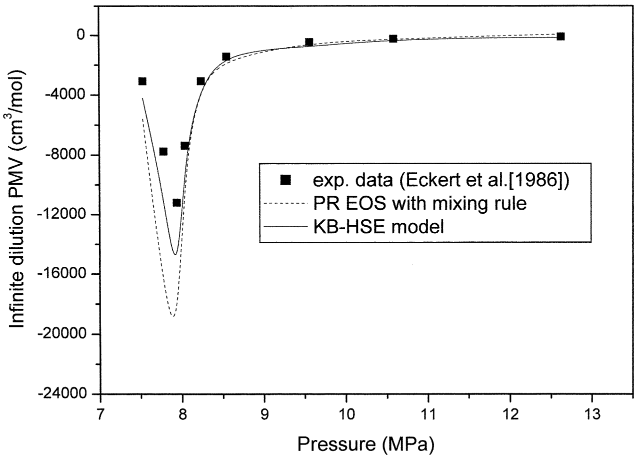

Fig. 1. Infinite dilution partial molar volume prediction of naphthalene in supercritical carbon dioxide at 307.2 K by the Peng-Robinson equation of state with the classical mixing rule and the KB-HSE fluctuation integral model.

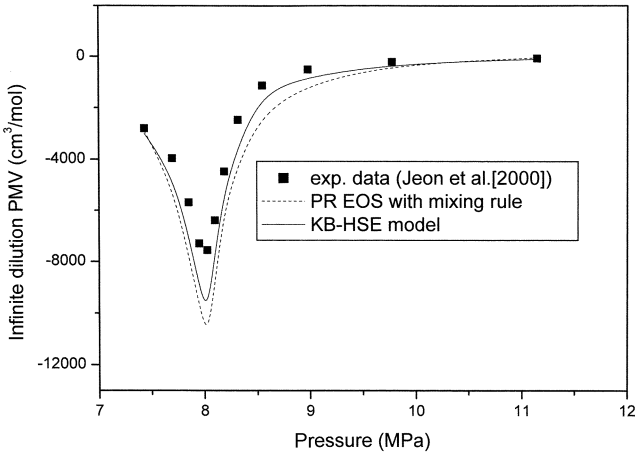

Fig. 2. Infinite dilution partial molar volume prediction of biphenyl in supercritical carbon dioxide at 308.2 K by the Peng-Robinson equation of state with the classical mixing rule and the KB-HSE fluctuation integral model.

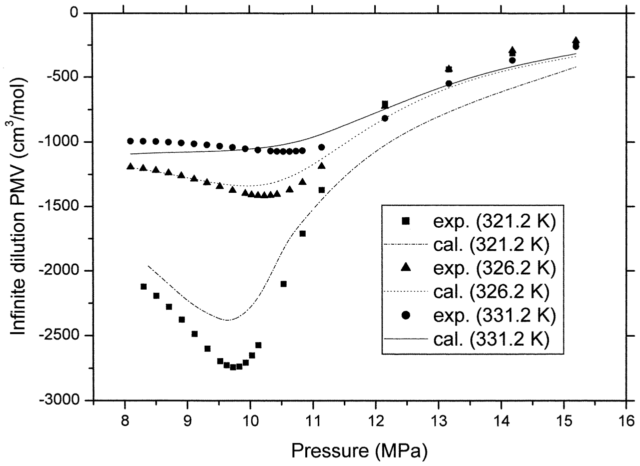

Fig. 3. Infinite dilution partial molar volume prediction of acenaphthylene in supercritical carbon dioxide at 321.2 K, 326.2 K, and 331.2 K by the KB-HSE fluctuation integral model.

KB-HSE fluctuation integral model is smaller than that by the Peng-Robinson equation of state with the classical mixing rule. Fig. 2 also shows the comparison of the infinite dilution PMV results of biphenyl in supercritical carbon dioxide with the experimental data published by our group [Jeon et al., 2000]. The results on other solutes in supercritical carbon dioxide are listed in Table 2, which shows the KB-HSE fluctuation integral model in this work provides improvement over the Peng-Robinson model in the overall, and especially near the critical point.

Even though there are two adjustable parameters (σ_{12}, α_{12}) in the KB-HSE fluctuation integral model compared with one adjustable parameter (k_{12}) in the Peng-Robinson model, the KB-HSE model has an advantage in that the model does not need three parameters, that is, two critical constants and acentric factor on the solute of interest.

The KB-HSE fluctuation integral model can be used to evaluate the infinite dilution PMVs of solutes whose critical constants are not well known because of difficulty in measuring critical properties due to decomposition before critical point. Fig. 3, for example, demonstrates the PMVs of acenaphthylene, whose critical properties are not available in the literature, in supercritical carbon dioxide predicted by the KB-HSE fluctuation integral model.

It is shown that the KB-HSE fluctuation integral model based on theoretical derivation can predict the partial molar volumes as well as solubilities of solutes in supercritical fluids with fewer parameters than the Peng-Robinson equation of state with an appropriate mixing rule.

CONCLUSIONS

Among three molecular parameters to evaluate the infinite dilution PMVs of solids in supercritical solvent by the KB-HSE fluctuation integral model in this work, only two parameters (σ_{12}, α_{12}) were optimized to fit the experimental infinite dilution PMVs with the value of the size parameter σ_{11} fixed as in the work on the solubility prediction of solutes in supercritical fluids [Kwon and Mansoori, 1993].

The overall results on the infinite dilution PMVs by the KB-HSE fluctuation integral method were compared with those by the Peng-Robinson equation of state with the classical mixing rule, and it was also shown that the KB-HSE fluctuation integral model produced better results than the Peng-Robinson equation of state with the clas-

Table 2. Prediction results of the infinite dilution partial molar volumes of various compounds in supercritical carbon dioxide

Carbon dioxide system	Temperature range (K)	Pressure range (bar)	No. of data	Peng-Robinson EOS (AAD^a)	KB-HSE model (AAD)	Data source
Naphthalene	307.2-372.2	74.6-373.0	41	39.3	31.0	Eckert et al. [1986)] Shim and Johnston [1991]
Phenanthrene	307.2-372.2	84.4-258.5	34	98.3	57.3	Shim and Johnston [1991]
Fluorene	308.2-313.2	70.0-110.0	21	67.9	54.2	Foster et al. [1989]
DHA ethyl ester	313.1-323.0	77.2-158.6	11	91.6	78.4	Liong et al. [1991]
DHA methyl ester	313.1	75.8-151.7	7	69.2	47.0	Liong et al. [1991]
EPA methyl ester	313.1-323.0	72.4-172.4	13	55.6	43.5	Li Liong et al. [1991]
Biphenyl	311.2-333.2	81.04-151.2	27	65.9	65.3	Jeon et al. [2000]
Acenaphthylene	311.2-333.2	81.04-151.2	36	-	26.8	Jeon et al. [1999]

^{a}AAD=average absolute deviation

sical mixing rule.

From the case of acenaphthylene, it is also concluded that the infinite dilution PMVs as well as solubilities of a solid in supercritical fluids can be predicted reasonably by the KB-HSE fluctuation integral method when critical properties of the solid are not well known.

ACKNOWLEDGEMENTS

This project is supported by the Kangwon National University Research Fund.

REFERENCES

Bader, M. S. H. and Gasem, K. A., "Prediction of Phase Behavior, Henry's Constants, and Infinite Partial Molar Volumes for Carbon Dioxide and Carbon Monoxide in n-Paraffins," *J. Supercritical Fluids*, **9**, 244 (1996).

Bartle, K. D., Clifford, A. A. and Shilstone, G. F., "Estimation of Solubilities in Supercritical Carbon Dioxide: A Correlation for the Peng-Robinson Interaction Parameters," *J. Supercritical Fluids*, **5**, 220 (1992).

Bharath, R., Inomata, H. and Arai, K., "Vapor-Liquid Equilibria for Binary Mixtures of Carbon Dioxide and Fatty Acid Ethyl Esters," *Fluid Phase Equilibria*, **50**, 315 (1989).

Brennecke, J. F. and Eckert, C. A., "Phase Equilibria for Supercritical Fluid Process Design," *AIChE J*., **35**, 1409 (1989).

Ben-Naim, A., "Inversion of the Kirkwood-Buff Theory of Solutions: Application to the Water-Ethanol System," *J. Chem. Phys*., **67**, 4884 (1977).

Carnahan, N. F. and Starling, K. E., "Equations of State for Non-attracting Rigid Spheres," *J. Chem. Phys*., **51**, 635 (1969).

Chialvo, A. A., "Solute-Solute and Solute-Solvent Correlations in Dilute Near-Critical Ternary Mixtures: Mixed Solutes and Entrainer Effects," *J. Phys. Chem*., **97**, 2740 (1993) .

Cochran, H. D., Lee, L. L. and Pfund, D. M., "Application of the Kirkwood-Buff Theory of Solutions to Dilute Supercritical Mixtures," *Fluid Phase Equilibria*, **34**, 219 (1987).

Coutsikos, Ph., Magoulas, K., Tassios, D., Cortesi, A. and Kikic, I., "Correlation and Prediction of Infinite-dilution Partial Molar Volumes of Organic Solutes in SC Carbon Dioxide using the Peng-Robinson Equation and PHCT Equation of State and the LCVM EOS/GE Model," *J. Supercritical Fluids*, **11**, 21 (1997).

Debenedetti, P. G., "Clustering in Dilute, Binary Supercritical Mixtures: A Fluctuation Analysis," *Chem. Eng. Sci*., **42**, 2203 (1987).

Foster, N. R., Macnaughton, S. J., Chaplin, R. P. and Wells, P. T., "Critical Locus and Partial Molar Volumes in Supercritical Fluids," *Ind. Eng. Chem. Res*., **28**, 2903 (1989).

Jeon, Y. P., Roth, M. and Kwon, Y. J., "Infinite Dilution Partial Molar Volume of Azulene and Acenaphthylene in Supercritical Carbon Dioxide," *J. Phys. Chem. B*, **103**, 8132 (1999).

Jeon, Y. P., Roth, M. and Kwon, Y. J., "Infinite Dilution Partial Molar Volume of Naphthalene and Biphenyl in Carbon Dioxide from Supercritical Fluid Chromatography: Composition Effects in the Stationary Phase," *J. Phys. Chem. A*, **104**, 5396 (2000).

Kim, H., Lin, H. M. and Chao, K. C., "Cubic Chain-of-Rotators Equation of State," *Ind. Eng. Chem. Fundamentals*, **25**, 75 (1986).

Kirkwood, J. G. and Buff, F. P., "The Statistical Mechanical Theory of Solutions," *J. Chem. Phys*., **19**, 774 (1951).

Kwon, Y. J., Lee, J. Y. and Kim, K. C., "Application of the Kirkwood-Buff Solution Formalism and the Hard Sphere Expansion Method with the Modified Mean Density Approximation to Predict Solubility of Solutes in Supercritical Fluids," *Korean J. Chem. Eng*., **14**, 184 (1997).

Kwon, Y. J. and Mansoori, G. A., "Solubility Modeling of Solids in Supercritical Fluids Using the Kirkwood-Buff Fluctuation Integral with the HSE Theory," *J. Supercritical Fluids*, **6**, 173 (1993).

Levelt Sengers, J. M. H., "Thermodynamic Behavior of Fluids in the Supercritical Region," *J. Supercritical Fluids*, **4**, 215 (1991).

Liong, K. K., Foster, N. R. and Yun, S. L. J., "Partial Molar Volumes of DHA and EPA Esters in Supercritical Fluids," *Ind. Eng. Chem. Res*., **30**, 569 (1991).

Liu, H. and Macedo, E., "A Study on the Models for Infinite Dilution Partial Molar Volumes of Solutes in Supercritical Fluids," *Ind. Eng. Chem. Res*., **34**, 2029 (1995).

Mansoori, G. A. and Leland, T. W., "Statistical Thermodynamics of Mixtures," *J. Chem. Soc. Faraday, Trans*., **68**, 320 (1972).

O'Connell, J. P., "Thermodynamic Properties of Solutions and the Theory of Fluctuations," *Fluid Phase Equilibria*, **6**, 21 (1981).

Peng, D.-Y. and Robinson, D. B., "A New Two Constant Equation of State," *Ind. Eng. Chem. Fundam*., **15**, 59 (1976).

Prausnitz, J. M., Lichenthaler, N. R. and Azevedo, E. G., *Molecular Thermodynamics of Fluid-Phase Equilibria*, Prentice-Hall, Englewood Cliffs, NJ (1986).

Reid, R. C., Prausnitz, J. M. and Poling, B. E., *The Properties of Gases and Liquids*, 4th ed., McGraw-Hill Book Co., New York (1987).

Schmitt, W. J. and Reid, R. C., "Solubility of Monofunctional Organic Solutes in Chemically Dispersed Supercritical Fluids," *J. Chem. Eng. Data*, **31**, 204 (1986).

Shin, G. S., Park, J. S. and Kwon, Y. J., "An Improved Conformal Solution Method Based on Hard Sphere Expansion to Predict Vapor-Liquid Equilibria," *Korean J. Chem. Eng*., **15**, 603 (1998).

Shim, J.-J. and Johnston, K. P., "Phase Equilibria, Partial Molar Enthalpies, and Partial Molar Volumes Determined by Supercritical Fluid Chromatography," *J. Phys. Chem*., **95**, 353 (1991).