

Determination of the Second Virial Coefficient for Binary Mixtures of Ar with CH₄ and CO using Van der Waals and Dieterici Models

M. Najafi^{1*} and E. Marzbanpour²

¹ Materials and Nuclear Fuel Research School, Nuclear Science and Technology Research Institute, Tehran, Islamic Republic of Iran

² Department of Chemistry, Payam Noor University, Abhar, Islamic Republic of Iran

Received: 26 February 2019 / Revised: 11 June 2019 / Accepted: 22 July 2019

Abstract

In this paper, we calculate the second virial coefficient for binary mixtures of Ar with CH₄ and CO in order to evaluate the performance of equations of state (EOSs). The investigated EOSs are van der Waals (vdW), Redlich-Kwong (RK), Peng-Robinson (PR), Carnahan-Starling–van der Waals (CS-vdW) and Guggenheim-van der Waals (G-vdW) based on van der Waals model. In our work, we also use Dieterici model of EOS consists of Dieterici (D) and Dieterici-Carnahan-Starling (DCS). In this study, the ability of these EOSs to predict second virial coefficients of binary mixtures is illustrated and since these models represent two different physical attitudes of contribution of interaction between molecules to thermodynamic functions, therefore from this view point, a comparison between the two models of equations of state is also reported.

Keywords: Van der Waals model; Dieterici model; Second virial coefficient; Binary mixtures.

Introduction

Thermophysical data on chemical compounds are essential for design of chemical industries. In this regard, prediction of such properties by using suitable models has fundamental importance. Equations of State (EOSs) are very suitable tools to do prediction of thermodynamic properties of gases, liquids or even solids in different temperatures and pressures[1-9].

The virial equation of state (VEOS) is likely the oldest theoretical tool for calculating the p - V - T properties of fluids

$$Z = 1 + \sum_{n=2} B_n \rho^{n-1} \quad (1)$$

in which ρ is the density ($\rho = 1/V_m$), Z is the compressibility factor ($Z = pV_m / RT$) and B_n is n th-virial coefficient. What is important is that the virial equation is obtained on the basis of statistical mechanics, since virial coefficients are related to intermolecular interactions. In this respect, the n th-virial coefficient is rigorously related to molecular interaction in clusters of n molecules. For example, the second virial coefficient is derived from the interaction of two molecules; the third one is the result of the effects of the triple molecular interactions, and so on. From this view point, the

* Corresponding author; Tel: 989128267426; Fax: 9888221116; Email: mnajafi@aeoi.org.ir

virial coefficients provide a critical bridge between macroscopic and microscopic properties and represent the non-ideal behavior of real gases. The thermophysical properties of fluids may be easily computed using virial equation of state and hence, accurate knowledge of the virial coefficients is of great significance [10-11].

Virial coefficients can be obtained from theoretical approaches and experimental measurements. Experimental measurements are such as *PVT*, speed of sound, Joule–Thomson, relative permittivity and so on. On the other side, virial coefficients can be calculated from theoretical approaches that usually consist of using equations of state and interaction potential functions [10-22].

In this paper, we calculate the second virial coefficient for binary mixtures of Ar with CH₄ and CO using several equations of state. In general, the *n*th-virial coefficient (*B_n*) can be obtained from any equation of state *via* the following relationship:

$$B_n = \frac{1}{(n-1)!} \left(\frac{\partial^{n-1} Z}{\partial \rho^{n-1}} \right)_{\rho=0} \quad (2)$$

Therefore the second virial coefficient is

$$B_2 = \left(\frac{\partial Z}{\partial \rho} \right)_{\rho=0} \quad (3)$$

The aim of this work is to investigate whether the two models of equations of state can be used to accurately predict the second virial coefficients of mixtures and also since these models represent two different physical attitudes of contribution of interaction between molecules to thermodynamic functions, we compare the two attitudes in this study and illustrate which model is better.

Equations of State

Historically, the development of equations of state has been largely empirical. However, EOSs are being formulated increasingly with the benefit of greater theoretical insights. In our work, we use five EOSs of van der Waals model and two EOSs of Dieterici model for calculating and predicting the second virial coefficient of binary mixtures of Ar with CH₄ and CO. The use of these EOSs has become widespread because of their advantages:

- Simplicity of application
- Only a few parameters need to be determined

In fact, the ease and speed of implementation combined with the precise results in many practical

cases explains why using these equations of state is still common in industrial applications and designs. At present, due to existence of various articles, the applications of these models to high pressure phase equilibria, to binary and multicomponent mixtures, to polymer mixtures, to reservoir fluids, and to supercritical fluids are well known [2-9].

Van der Waals Model

The van der Waals EOS, proposed in 1873 in his doctoral thesis, was the first equation to predict vapor-liquid coexistence [23]

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2} \quad (4)$$

The parameters *a* and *b* are related to attractive forces between the molecules and the covolume occupied by the molecules respectively. They can be obtained from the critical properties of fluid. In the spirit of vdW equation, equation of state in the literature almost invariably follows the "repulsive + attractive" formula, *i.e.*

$$p = p_{rep} + p_{att} \quad (5)$$

or

$$Z = Z_{rep} + Z_{att} \quad (6)$$

in which the subscripts identify the contributions of intermolecular repulsion and attraction forces to pressure or compressibility factor. Van der Waals model is the first one for calculation and prediction of thermophysical properties of fluids based on attractive and repulsive forces. Many of the equations of state that have been introduced later, with different degree of success for non-ideal liquids and gases, are based on this model [1-3]. Many of them can be categorized in terms of modifications to the repulsive and attractive of vdW model.

Five EOSs based on vdW model have been used in this paper for calculating and predicting the second virial coefficient of binary mixtures of Ar with polar and non-polar fluids and the details are shown in Table 1.

Dieterici Model

In 1899, Dieterici suggested an EOS involving an exponential term [24]

$$p = \frac{RT}{V_m - b} e^{-a/RTV_m} \quad (7)$$

This model can be generalized as follows

Table 1. The models used in this work

Model	EOS	Formula	a	b
vd Waals	Van der Waals (vdW)	$Z = \frac{V_m}{V_m - b} - \frac{a}{RTV_m}$	$27 R^2 T_c^2 / 64 P_c$	$RT_c / 8 P_c$
	Redlich-kwong (RK)	$Z = \frac{V_m}{V_m - b} - \frac{a}{RT^{0.5}(V_m + b)}$	$0.4278 R^2 T_c^{2.5} / P_c$	$0.0867 RT_c / P_c$
	Peng-Robinson (PR)	$Z = \frac{V_m}{V_m - b} - \frac{a(T)V_m}{RT[V_m(V_m + b) + b(V_m - b)]}$	$45724(R^2 T_c^2 / P_c) \{1 + k[1 - (T/T_c)^{0.5}]\}^2$	$0.07780 RT_c / P_c$
	Guggenheim (G-vdW)	$Z = \frac{1}{(1-\eta)^4} - \frac{a}{RTV_m}, \eta = \frac{b}{4V_m}$	$0.49002 R^2 T_c^2 / P_c$	$0.18284 RT_c / P_c$
	Carnahan-Starling (Cs-vdW)	$Z = \frac{1 + \eta + \eta^2 - \eta^3}{(1-\eta)^3} - \frac{a}{RTV_m}, \eta = \frac{b}{4V_m}$	$0.4963 R^2 T_c^2 / P_c$	$0.18727 RT_c / P_c$
Dieterici	Dieterici(D)	$Z = \frac{V_m}{V_m - b} e^{-a/RTV_m}$	$0.5411 R^2 T_c^2 / P_c$	$RT_c / e^2 P_c$
	Dieterici-Carnahan-starling(DCS)	$Z = \frac{(1 + \eta + \eta^2 - \eta^3)}{(1-\eta)^3} e^{-a/RTV_m}, \eta = \frac{b}{4V_m}$	$0.8143 R^2 T_c^2 / P_c$	$1.5285 V_c$

$$Z = Z_{rep} e^{Z_{att}} \quad (8)$$

Despite some advantages such as a more realistic critical compressibility factor ($Z^c = 0.2706$), the Dieterici's equation has not contributed significantly to the development of modern equations of state.

The same as van der Waals EOS, attractive or repulsive term of Dieterici EOS can be replaced with the other terms. In this respect, Sadus replaced the repulsive term of this model with the Carnahan-Starling expression and observed the generally good results on predicting the phase behavior of some fluids and binary mixtures [25-26]. Therefore, the generalized Dieterici formula can be used the basis for equation of state development.

Two EOSs on the basis of Dieterici model have

been used in our work for calculating and predicting the second virial coefficient of binary mixtures of Ar with polar and non-polar fluids and the details are shown in Table 1.

Results and Discussion

In this paper, we used five vdW EOSs and two EOSs based on Dieterici model for calculating and predicting second virial coefficient for binary mixtures of Ar with CH₄ and CO. Table 2 gives critical properties and acentric factors of the fluids. For determining parameters a and b of EOSs for mixtures, the classical van der Waals mixing rules were used as follows

Table 2. Critical properties and acentric factors of fluids

Fluid	T_c (K)	P_c (atm)	ρ_c (mol/L)	ω	D (Debye)
Ar	150.687	47.994	13.4074	0.0022	0.0
CO	132.86	34.478	10.85	0.05	0.1
CH ₄	190.564	45.391	10.139	0.01142	0.0

$$a = \sum_i \sum_j x_i x_j a_{ij} \tag{9}$$

$$b = \sum_i x_i b_i$$

with

$$a_{ij} = \sqrt{a_i a_j} (1 - k_{ij}) \tag{10}$$

where x_i is the mole fraction of i and equals to 0.5 in this work and k_{ij} is the binary interaction parameter.

Figures 1 and 2 show the calculated second virial coefficient of binary mixtures versus temperature using the above mentioned EOSs. In these figures, the obtained results are compared with the experimental data [27-30]. By reviewing the figures, we obtain the following results:

1- All EOSs predict the qualitative behavior of the second virial coefficient of mixtures in respect to the temperature. But quantitatively, each of EOS presents different results.

2- In the very low temperature, Dieterici model

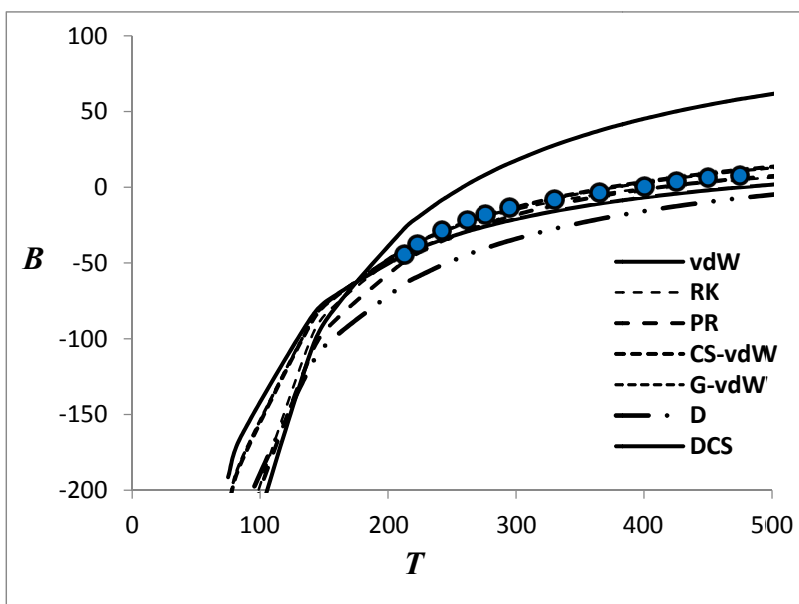


Figure 1. The calculated second virial coefficient of Ar-CO versus temperature

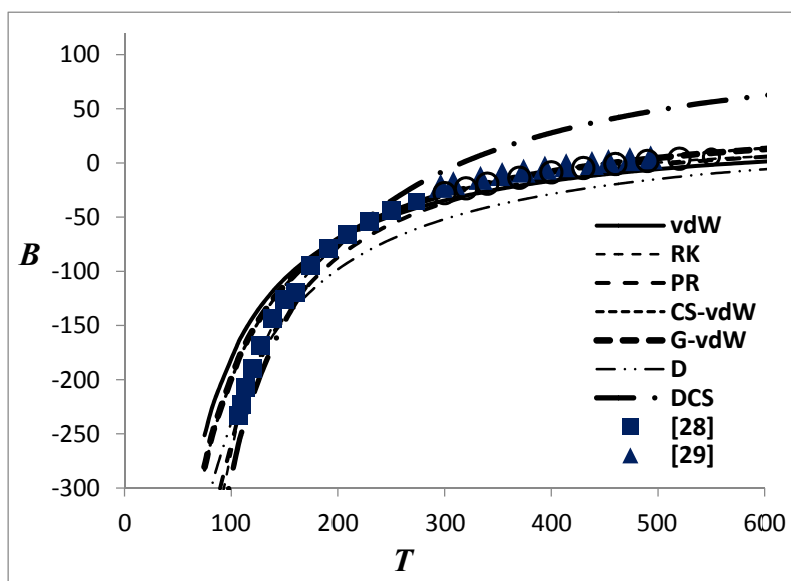


Figure 2. The calculated second virial coefficient of Ar-CH₄ versus temperature

provide consistent with experimental data, but at the medium and high temperature, this model shows a large deviation.

3- The EOSs on the basis of vdW model present more accurate results and these are consistent well with experimental data in wide range of temperatures.

4- Our study show RK and then PR equations of state predict very accurate results for the mixtures.

5- In Dieterici model, DCS shows a large deviation and D provides a fairly good results in high temperature in comparison with experimental data.

Conclusion

The obtained results show that all EOSs predict the qualitative behavior of the second virial coefficient of fluid mixtures in respect to the temperature but quantitatively, each of EOS presents different results in comparing with experimental data.

Quantitatively, it seems that vdW model yields very better prediction than Dieterici model in wide range of temperatures. In this respect, RK EOS provides very good consistent with experimental data for studied binary mixtures.

Given that these models represent two different physical attitudes of contribution of interaction between molecules to thermodynamic functions, it can be concluded that vdW model demonstrates the contribution better than the other. In fact, it seems that the "repulsive + attractive" formula to pressure or compressibility factor are more in keeping with attitude of the system.

Acknowledgment

The authors express their appreciations to Nuclear Science and Technology Research Institute (NSTRI) for supporting this work.

References

1. Wei Y.S. and Sadus R. J., Equations of state for the calculation of fluid-phase equilibria, *AIChE J.*, **46**:169(2000).
2. Valderrama J. O., The State of the Cubic Equations of State, *Ind. Eng. Chem. Res.*, **2**:1603(2003).
3. Guevara-Rodriguez F de J., A methodology to define the Cubic Equation of State of a simple fluid *Fluid Phase Equilib.*, **307**:190(2011).
4. Guennec Y. L., Privat R., Lasala S. and Jaubert J., On the imperative need to use a consistent α -function for the prediction of pure-compound supercritical properties with a cubic equation of state, *Fluid Phase Equilib.*, **445**:45(2017).
5. Ghoderao P. N. P., Dalvi V. H. and Narayan M., A four-parameter cubic equation of state for pure compounds and mixtures, *Chem. Eng. Sci.*, **190**:173(2018).
6. Forero L. and Velásquez J. A., A generalized cubic equation of state for non-polar and polar substances, *Fluid Phase Equilib.*, **418**:47(2016).
7. Coelho J. A. P., Filipe R. M. and Naydenova G. P., Semi-empirical models and a cubic equation of state for correlation of solids solubility in ScCO₂: Dyes and calix[4]arenes as illustrative examples, *Fluid Phase Equilib.*, **426**:37(2016).
8. Guevara-Rodriguez F. de J. and Romero-Martinez A., An empirical extension for a generalized cubic equation of state, applied to a pure substance with small molecules, *Fluid Phase Equilib.*, **347**:22(2013).
9. Glass M., Djelassi H. and Mitsos A., Parameter estimation for cubic equations of state models subject to sufficient criteria for thermodynamic stability, *Chem. Eng. Sci.*, **192**:981(2018).
10. Meng L., Duan Y-Y and Lei Li, Correlations for second and third virial coefficients of pure fluids *Fluid Phase Equilib.*, **226**:109(2004).
11. Assael M. J., Trusler J.P.M. and Tsolakis T. F., *An introduction to their Prediction Thermophysical Properties of Fluids*, Imperial College Press, London, UK, (1996).
12. Van Tat P. and Deiters U. K., Calculation of cross *second virial coefficients* using ab initio intermolecular potential energy surfaces for dimer H₂-N₂, *Chem. Phys.*, **517**:208(2019).
13. Pérez-Polo M. F., Pérez-Molina M., Varó E. F. and Chica J., Estimation of the virial coefficients by means of chaotic oscillations of pressure and density: Application to quantum gases with cubic equations of state, *Fluid Phase Equilib.*, **473**:262(2018).
14. Peyrovedin H., Esmailzadeh F. and M. Binazadeh, Calculation of the second virial coefficient and molecular radius of polar and non-polar substances using a new potential function, *Fluid Phase Equilib.*, **492**:88(2019).
15. Di Nicola G., Coccia G., Pierantozzi M. and Falone M., A semi-empirical correlation for the estimation of the *second virial coefficients* of refrigerants, *Int. J. Refrigeration*, **68**:242(2016).
16. Mamedov B. A. and Somuncu E., Accurate calculation of *second virial coefficient* of the Exp-6 potential and its application, *Physica A: Statistical Mechanics and its Applications*, **420**:246(2015).
17. Khoshshima A. and Hosseini A., Prediction of the Boyle temperature, *second virial coefficient* and Zeno line using the cubic and volume – translated cubic equations of state, *J. Mol. Liq.*, **242**:625(2017).
18. Bonneville R., Asymptotic expression of the virial coefficients for hard sphere systems, *Fluid Phase Equilib.*, **397**:111(2015).
19. Yin J. and Wu J., Gas phase PVT properties and second virial coefficients of dimethyl ether, *Fluid Phase Equilib.*, **298**:298(2010).
20. Gámez F., Numerical evaluation of the *second virial coefficients* of anisotropic multipolar intermolecular potentials, *J. Mol. Liq.*, **220**:731(2016).
21. Shaheen M. E., Ghazy A. R., Kenawy E. and El-Mekawy

- F., Application of laser light scattering to the determination of molecular weight, *second virial coefficient*, and radius of gyration of chitosan, *Polymer*, **158**:18(2018).
22. Vtulkina E. D. and Elfimova E. A., Fourth and fifth virial coefficients and thermodynamic properties of the dipolar hard sphere fluids in zero external magnetic field, *Fluid Phase Equilibri.*, **417**:109(2016).
23. Van der Waals J. D., *On the Continuity of the Gaseous and Liquid State Doctoral Dissertation*, University of Leiden, Holland, (1873).
24. Polishuk I., Gonzalez R., Verab J. H. and Segura H., Phase behavior of Dieterici fluids, *Phys. Chem. Chem. Phys.*, **6**:5189(2004).
25. Sadus R. J., Equations of state for fluids: The Dieterici approach revisited, *J. Chem. Phys.*, **115**:1460(2001).
26. Sadus R. J., New Dieterici-type equations of state for fluid phase equilibria, *Fluid Phase Equilibri.*, **212**:31(2003).
27. Dymond J. H., and Smith E. B., *The Virial Coefficients of Pure Gases and Mixtures: A Critical Compilation*, Clarendon Press Oxford (1980)
28. Byrne M. A., Jones M. R. and Staveley L. A. K., Second virial coefficients of argon, krypton and methane and their binary mixtures at low temperatures, *Trans. Faraday Soc.*, **64**:1747(1968).
29. Strein K., Lichtenthaler R. N., Schramm B. and Schafer K., Meßwerte des zweiten Virialkoeffizienten einiger gesättigter Kohlenwasserstoffe von 300—500 K, *Ber. Bunsenges. Phys. Chem.*, **75**:1308(1971).
30. Bellm J., Reineke W., Schafer K. and Schramm B., Messungen zweiter Virialkoeffizienten im Temperaturbereich von 300–550 K, *Ber. Bunsenges. Phys. Chem.* **78**:282(1974).