

An Improved Extended-Corresponding-States Theory for Natural Gas Mixtures¹

I. M. Marrucho,² A. M. F. Palavra,² and J. F. Ely^{3,4}

In this work the van der Waals one-fluid extended-corresponding-states theory mixing rules are modified so that the composition dependence of the second virial coefficient is theoretically correct, regardless of the mixing rules used to describe the remainder of the pVT surface. This modification leads to a substantial improvement in the prediction of the mixture phase equilibrium. Results and comparisons with the unmodified extended-corresponding-states theory and experimental data are presented.

KEY WORDS: corresponding states; mixing rules; natural gases; second virial coefficients.

1. INTRODUCTION

The reliable modeling of mixture thermophysical property behavior includes an accurate description of both bulk and phase equilibrium properties. Ideally, both these needs should be met by a single model. To this date, however, no single mixture model has been proposed which can represent both these types of properties with high accuracy. Thus, it is common to use one model for bulk-phase properties (e.g., the extended corresponding states or AGA-8 for natural gases) and a different model to define phase boundaries (e.g., the Peng–Robinson model for hydrocarbons).

In this work we reformulate the van der Waals one-fluid extended-corresponding-states theory mixing rules so that a single model can be used to describe natural gas mixtures. Extended corresponding states for mixtures was originally proposed by Leland and co-workers [1, 2] and has

¹ Paper presented at the Twelfth Symposium on Thermophysical Properties, June 19–24, 1994, Boulder, Colorado, U.S.A.

² Instituto Superior Tecnico, Lisbon, Portugal.

³ Colorado School of Mines, Golden, Colorado 80401, U.S.A.

⁴ To whom correspondence should be addressed.

been modified to include exact shape factors by Ely *et al.* [3]. This model has been used successfully to calculate bulk properties of an extensive range of mixtures, including natural gases, but the incorrect compositional mapping on the vapor side leads to a less than satisfactory description of the phase equilibrium in these systems. This behavior is traceable to the composition dependence of the second virial coefficient which is generated in the van der Waals one-fluid theory.

In this work, new mixing rules are introduced so that the statistical-mechanical second-virial-coefficient composition dependence is recovered. The results for phase equilibrium properties are compared with the one-fluid van der Waals theory and experimental results for mixtures of natural gases.

2. EXTENDED CORRESPONDING STATES

The extended-corresponding-states theory (ECST) is one of the most successful models in predicting saturated liquid densities of natural gas [4] and ethane + propane mixtures [5], even relatively close to the mixture critical point. The accuracy of this approach lies in the accuracy of the empirical reference-fluid equation of state and the accuracy of the shape factors which are used to define the equivalent state point of the reference fluid. The two basic equations that conformal substances must obey in this theory are

$$\frac{A_j^r(\rho_j, T_j)}{RT_j} = \frac{A_0^r(\rho_0, T_0)}{RT_0} \quad (1)$$

$$Z_j^r(\rho_j, T_j) = Z_0^r(\rho_0, T_0)$$

In these equations A^r is the residual Helmholtz energy, Z^r the residual compressibility factor, ρ the molar density, T the absolute temperature, and the subscripts "j" and "0" indicate the target fluid of interest (pure or mixture) and the reference fluid, respectively. The mapping of these thermodynamic functions between the two fluids is achieved by the definition of equivalent-substances reducing ratios, f_j and h_j :

$$T_0 = T_j/f_j \quad (2)$$

$$\rho_0 = h_j\rho_j$$

and

$$f_j(\rho_j, T_j) = (T_j^c/T_0^c) \theta_{j0}(\rho_j, T_j) \quad (3)$$

$$h_j(\rho_j, T_j) = (\rho_0^c/\rho_j^c) \phi_{j0}(\rho_j, T_j)$$

where the superscript “c” denotes the critical property and θ and ϕ the shape factors. The shape factors are functions of the density and temperature and can be seen as slowly distorting scales that force the two fluids to conformality. They are calculated by simultaneously solving the system of Eqs. (1).

The extension of this model to mixtures is usually done by using the conventional van der Waals one-fluid (VDW-1) mixing rule approach:

$$f_x(\rho_x, T_x, \{x_i\}) = h_x(\rho_x, T_x, \{x_i\})^{-1} \sum_i \sum_j x_i x_j h_{ij}(\rho_x, T_x) f_{ij}(\rho_x, T_x) \tag{4}$$

$$h_x(\rho_x, T_x, \{x_i\}) = \sum_i \sum_j x_i x_j h_{ij}(\rho_x, T_x)$$

and

$$f_{ij} = (f_i f_j)^{1/2} (1 - k_{ij}) \tag{5}$$

$$h_{ij} = \frac{1}{8} (h_i^{1/3} + h_j^{1/3}) (1 - l_{ij})$$

The subscript “x” denotes a mixture property, x_i designates the mole fraction of component i in the mixture, and k_{ij} and l_{ij} the interaction parameters that are usually considered constants for the system of interest. The f_i and h_i are defined in Eq. (2). In this way, the properties of a mixture can be calculated from the knowledge of pure component and reference fluid properties at the equivalent state point.

3. PHASE EQUILIBRIUM

The phase equilibrium in mixtures is described by the equilibrium K -values which are defined by the ratio of the fugacity coefficients of component i in the liquid phase, $\hat{\phi}_i^l$, and vapor phase, $\hat{\phi}_i^v$:

$$K_i = \hat{\phi}_i^l / \hat{\phi}_i^v \tag{6}$$

The $\hat{\phi}_i^v$'s are evaluated in terms of the thermodynamic properties of the reference fluid according to the following equations:

$$\ln \phi_i = \ln \phi_0 + z_0^r H_{mi} + u_0^r F_{mi} \tag{7}$$

$$\ln \phi_0 = a_0^r + z_0^r - \ln z_0$$

where $\hat{\phi}_i$ and ϕ_0 are the fugacity coefficients of component i and the reference fluid, and a_0^r , z_0^r , and u_0^r are the dimensionless residual Helmholtz energy (A^r/RT), the residual compressibility factor ($Z - 1$), and dimensionless

residual internal energy of the reference fluid (U^r/RT), respectively. The quantities H_{ni} and F_{ni} are the dimensionless composition derivatives defined as

$$\begin{aligned} H_{ni} &= \frac{n}{h_x} \left(\frac{\partial h_x}{\partial n_i} \right)_{T, \rho, n_j \neq n_i} \\ F_{ni} &= \frac{n}{f_x} \left(\frac{\partial f_x}{\partial n_i} \right)_{T, \rho, n_j \neq n_i} \end{aligned} \quad (8)$$

In this work a 32-term modified Benedict-Webb Rubbin (MBWR-32) equation of state for propane was chosen to represent the reference fluid. Since the shape factors perform an exact mapping between pure fluids, the choice of the reference fluid is not important provided that the fluid chosen spans an appropriate range of reduced temperatures and pressures. The higher-order temperature and density dependence of the reference fluid equation of state provides a nearly exact description of the bulk-phase properties. Unfortunately, the fact that the van der Waals one-fluid extended-corresponding-states theory only scales correctly terms up to $1/T$ [6] makes this approach incorrect. Until now, most attempted improvements to the VDW-1 model have been focused on improving mixing rules for the liquid side.

To describe the behavior of gases accurately, the truncated version of the virial expansion is usually used. The reason for this choice is that it has a firm statistical-mechanical basis and the virial coefficients of a multicomponent mixture can be obtained from the component virial coefficients by formally rigorous mixing rules. The virial equation of state truncated after the first order in density has the form

$$Z_{\text{mix}} = 1 + B_{\text{mix}}(T) \rho_{\text{mix}} \quad (9)$$

where Z_{mix} and $B_{\text{mix}}(T)$ are the mixture density and second virial coefficient, respectively. The mixture second virial coefficient can be calculated from the second virial of the reference fluid as

$$B_{\text{mix}}(T, \{x_i\}) = \sum_i \sum_j x_i x_j h_{ij} B_0 \left(\frac{T}{f_{ij}} \right) \quad (10)$$

where f_{ij} is independent of composition. In the MBWR-32 equation of state the second virial B_0 is given as a cubic function of the inverse temperature:

$$B_0 = N_1 + N_2/T^{1/2} + N_3/T + N_4/T^2 + N_5/T^3 \quad (11)$$

Although the second virial for the reference fluid incorporates only 5 of the 32 terms in the equation of state, it is responsible for almost 90% of the

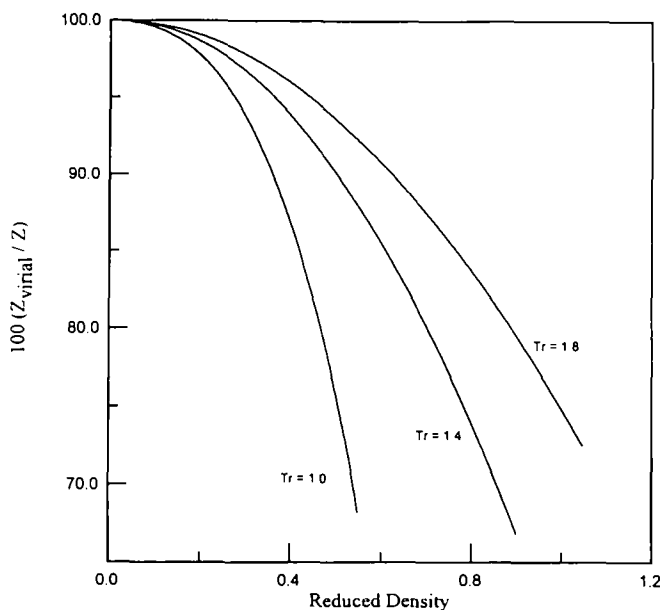


Fig. 1. Contribution of the second virial coefficient to the compressibility factor.

thermodynamic properties of the vapor mixtures [7] as illustrated in Figs. 1 and 2. Thus, errors in the VDW-1 representation of the second virial coefficient will be reflected as an erroneous description of the vapor-phase fugacity coefficient, Eq. (7).

The mixture second virial from the ECST is calculated by means of

$$B_{\text{mix}}^{\text{ECST}} = h_x B_0 \left(\frac{T}{f_x} \right) = \sum_i \sum_j x_i x_j h_{ij} B_0 \left(\frac{T}{f_x} \right) \quad (12)$$

where f_x is defined in Eq. (4). Comparing Eqs. (10) and (12) it can be concluded that this last expression is valid only if for all pairs $f_x = f_{ij}$. It is obvious that this is valid only for $i = j$ or if the second virial coefficient has a linear temperature dependence. This is not the case when the MBWR-32 is used to describe the properties of the reference fluid. Also note that the second virial coefficient from ECST does not have the quadratic composition dependence required by theory, since f_x introduces an additional composition dependence. Figure 3 illustrates this "artificial" composition dependence in the cross-virial coefficient obtained from the corresponding-states calculations.

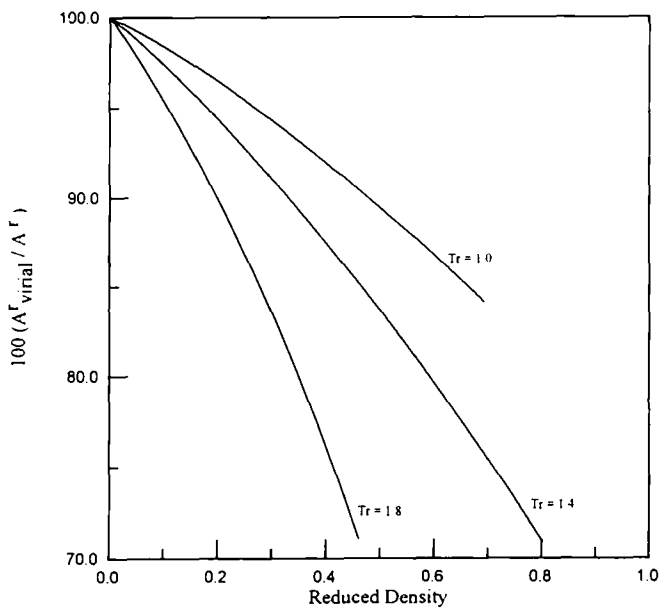


Fig. 2. Contribution of the second virial coefficient to the Helmholtz energy.

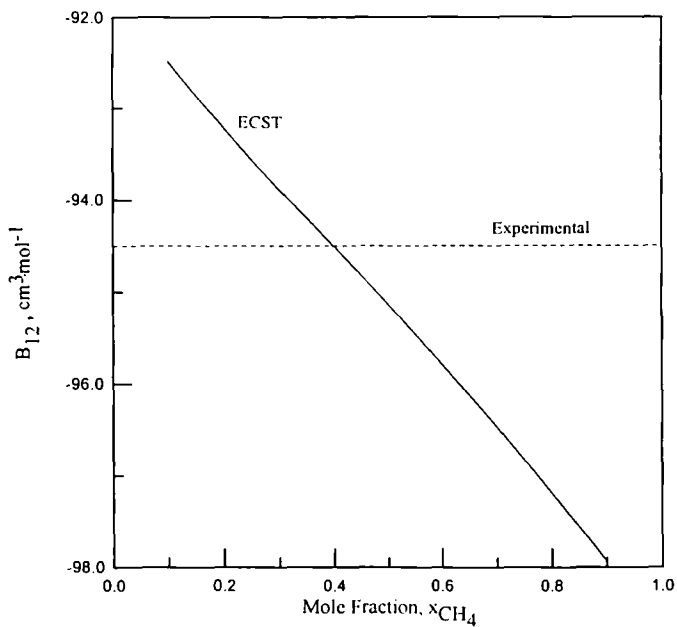


Fig. 3. Composition dependence of the ECST cross second virial coefficient for the mixture methane + ethane at 293.15 K.

In an effort to fix this deficiency, we have explored a new set of mixing rules based on the ideas of Wong-Sandler [8]. In particular, we have modified the volume mixing rule to be correct in the second virial limit:

$$\begin{aligned} f_x h_x^{\text{VDW}} &= \sum_i \sum_j x_i x_j f_{ij} h_{ij} \\ h_x^{\text{VDW}} &= \sum_i \sum_j x_i x_j h_{ij} \\ h_x^{\text{VIRIAL}} &= \sum_i \sum_j x_i x_j \frac{B_{ij}(T)}{B_0(T)/f_x} \end{aligned} \quad (13)$$

where B_{ij} is the second virial coefficient of the ij pair in the mixture. These mixing rules improve substantially the description of phase equilibrium properties, like K values, even for mixtures which exhibit relatively small size differences.

4. RESULTS

This modified ECST approach was used to calculate the equilibrium K values of the systems methane + ethane, methane + propane, methane + n -butane, and methane + n -pentane since these are the main components of most of the natural gas mixtures. In evaluating the pure B_{ii} in Eq. (13), the pure fluid MBWR-32 equations contained in the DDMIX program were used. The unlike cross virial B_{ij} were obtained from Ref. 9.

Figure 4 illustrates the results obtained for the methane K value in the systems mentioned above. As shown in this figure the new method consistently improves the description of the K values, except in the methane + n -butane. In this case we note that the modified ECST model is in perfect agreement with Peng-Robinson model, thus casting some doubts on the experimental data. An unwanted side effect of these mixing rules is a loss of accuracy in the ECST prediction of the liquid-phase properties. A possible way of recovering liquid phase one-fluid van der Waals ECST results is through a switching function:

$$h_x = \zeta h_x^{\text{VIRIAL}} + (1 - \zeta) h_x^{\text{VDW}} \quad (14)$$

where ζ is a switching function that is essentially zero or one according to the cutoff parameter chosen. This type of approach has been used in the past to switch between scaled and mean-field equations of state near the pure fluid critical point and in early wide-range equation-of-state development. It is also well-known that it will lead to a discontinuity in the derived properties, but since the bulk-phase properties are well represented in ECST this discontinuity is expected to be small.

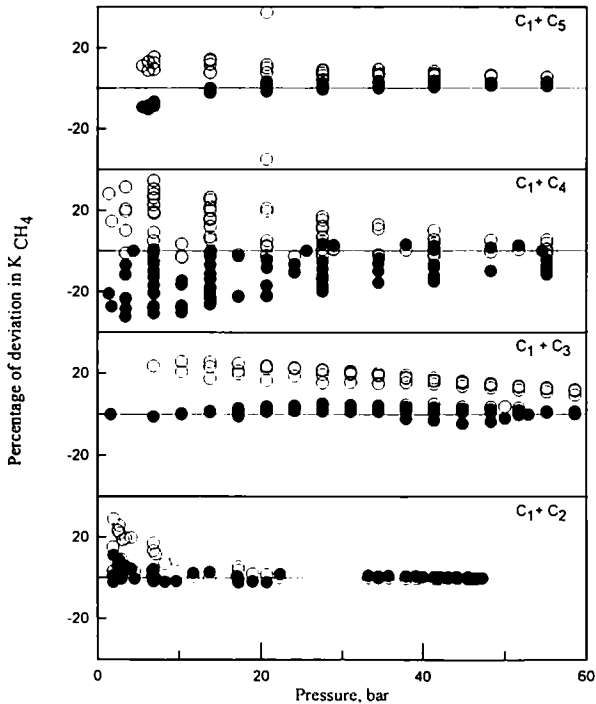


Fig. 4. Percentage of error in K_1 calculated from ECST and the model proposed in this work, for the mixtures (1)methane + (2)ethane (data in Refs. 10 and 11), (1)methane + (2)propane (data in Refs. 10 and 12), (1)methane + (2)*n*-butane at 199.88 K (data in Refs. 10 and 13) and (1)methane + (2)*n*-pentane (data in Ref. 14). (●) This work; (○) ECST.

5. CONCLUSIONS

In conclusion, we have demonstrated a weakness in the van der Waals one-fluid theory representation of the second virial coefficient which impairs its ability to represent accurately the phase equilibrium in natural gases. We have presented a promising approach to solve this problem which incorporates the correct composition dependence of the second virial coefficient in the mixing rules. Preliminary tests show that this modification markedly improves the methane K value in binary natural gas mixtures. Switching functions are currently being studied to improve the liquid-phase-bulk properties obtained with this model.

ACKNOWLEDGMENTS

I. M. Marrucho thanks JNICT, Programa Ciencia, BD\1534\91-RM, for the financial support. J. F. Ely was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, under Grant DE-FG02-92ER14294.

REFERENCES

1. J. W. Leach, P. S. Chappellear, and T. W. Leland, *AIChE J.* **14**:568 (1968).
2. T. W. Leland and P. S. Chappellear, *Ind. Eng. Chem. Fundam.* **60**:16 (1968).
3. J. F. Ely, W. M. Haynes, and B. C. Bain, *J. Chem. Thermodyn.* **21**:879 (1989).
4. R. D. McCarty, *J. Chem. Thermodyn.* **14**:837 (1982).
5. W. R. Parrish, *Fluid Phase Equil.* **18**:279 (1984).
6. M. L. Huber and J. F. Ely, Properties of Lennard-Jones Mixtures at Various Temperatures and Energy Ratios With a Size Ratio of Two, NIST TN-1331 (1989).
7. Dale D. Erickson, *A Method for Improving Equations of State Near the Critical Point*, Ph.D. thesis (Rice University, Houston, 1988).
8. D. A. H. Wong and S. I. Sandler, *AIChE J.* **38**(5):671 (1992).
9. R. C. Reid, J. M. Prausnitz, and B. E. Poling, *The Properties of Gases and Liquids*, 4th ed. (McGraw-Hill, New York, 1987).
10. M. Jaeschke, S. Van Caneghem, A. E. Humphreys, R. J. V. Rosmalen, Q. Pellei, J. P. J. Michels, J. A. Schouten, and C. A. Ten Seldam, High Accuracy Compressibility Factor Calculation for Natural Gases and Similar Mixtures by Use of a Truncated Virial Equation, GERG Technical Monograph 2 (1988).
11. I. Wichterle and R. Kobayashi, *J. Chem. Eng. Data* **17**(1):9 (1972).
12. H. H. Reamer, B. H. Sage, and W. N. Lacey, *Ind. Eng. Chem.* **42**(3):534 (1950).
13. G. D. Elliot, J. J. R. Chen, P. S. Chappellear, and R. Kobayashi, *J. Chem. Eng. Data* **19**(1):71 (1974).
14. B. H. Sage and W. N. Lacey, *Ind. Eng. Chem.* **30**(11):1296 (1938).