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Equation of State for Nonpolar Fluid Mixtures: Prediction from Boiling Point Constants

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Our previous corresponding-states correlation for the second virial coefficient of nonpolar fluids, based on the normal boiling point parameters, has been employed to predict the equation of state of nonpolar fluid mixtures. The analytical equation of state is that of Ihm, Song, and Mason, which requires three temperature-dependent parameters, i.e., the second virial coefficient, a scaling constant for softness of repulsive forces, and a van der Waals covolume. In the previous work, we showed that the temperature-dependent parameters could be calculated by knowing the boiling point constants. In this work, it is shown that using a simple geometric mean for the boiling point temperature and an arithmetic mean for the liquid density at the normal boiling point is sufficient to determine the temperature-dependent parameters for mixtures. The equation of state has been utilized to calculate the liquid density of several nonpolar fluid mixtures. The agreement with experiment is good.

KEY WORDS: compressed fluids; corresponding states; equation of state; second virial coefficient.

1. INTRODUCTION

The thermodynamic properties of fluids and fluid mixtures are important in model development and engineering applications. Although reliable experimental data may be preferable to values obtained by estimation methods, all too often reliable experimental data are not available. A central problem in the theory of fluids and fluid mixtures is the explanation of their thermodynamic properties in terms of intermolecular forces. One of the fundamental approaches to this problem is through the formulation of an accurate

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equation of state, whereby the thermodynamic functions can be easily determined.

The most significant theoretical advances in recent years have been the development of statistical–mechanical perturbation theories [1, 2], which are based on the recognition that the structure of a dense fluid is determined primarily by the intermolecular repulsive forces. The hard-sphere fluid can thus be taken as a reference system, and the influence of attractive forces and the softness of repulsions can be considered as perturbations.

Work by Ihm, Song, and Mason on the statistical–mechanical theory of the equation of state for fluids has yielded accurate results for both pure liquids [3–5] and their mixtures [6–8]. Knowing the intermolecular forces, one may employ this equation of state. However, the equation can be used with less input information than the full intermolecular forces [9]. Very recently, we proposed an empirical corresponding-states correlation for the second virial coefficient of nonpolar fluids [10]. In particular, we have shown that two scaling constants, the normal boiling point temperature (to make a dimensionless temperature) and the liquid density at the boiling point (to form a dimensionless second virial coefficient), are sufficient to correlate the second virial coefficient of nonpolar fluids with reasonable accuracy. We have employed this correlation to predict the equation of state of a large number of nonpolar fluids including noble gases, diatomic molecules, saturated hydrocarbons, and a number of aliphatic, aromatic, and cyclic hydrocarbons [10]. The purpose of this work is to extend the method for predicting the equation of state to nonpolar fluid mixtures.

2. THEORY

Starting from the pressure equation [11] and applying the Weeks–Chandler–Andersen [2] decomposition of the potential energy function, Song and Mason [3, 4] obtained an analytical equation of state of the form

$$\frac{p}{\rho kT} = 1 - \frac{(\alpha - B_2)\,\rho}{1 + 0.22\lambda b\rho} + \frac{\alpha\rho}{1 - \lambda b\rho} \tag{1}$$

for nonpolar and slightly polar fluids. Here p is the pressure, ρ is the molar (number) density, B_2 is the second virial coefficient, α is the contribution of the repulsive forces to the second virial coefficient, b is a temperature-dependent parameter analogous to the van der Waals covolume, kT is the thermal energy of one molecule, and λ is an adjustable parameter. The parameters B_2, α, and b are all temperature dependent and can be evaluated by knowing the intermolecular forces. However, such forces are almost never known with sufficient accuracy, except for noble gases [12]. In fact, it is shown that there is no need to specify the potential energy function, because knowledge of experimental second virial coefficient data is sufficient to determine the other two temperature-dependent parameters, α and b, by suitable scaling constants. Song and Mason [3, 13] showed that the experimental second virial coefficient data can be used to calculate the Boyle temperature and the Boyle volume. The Boyle volume can be used as a source of the scaling constant for reducing α and b, and the Boyle temperature can be used for reducing temperature. When reduced in this manner, the dimensionless plots of α/v_{B} and b/v_{B} vs T/T_{B} are universal functions, and empirical formulas [13] and numerical tables [5] for these parameters are available.

Another alternative to remedy this difficulty is the prediction of the second virial coefficients using corresponding-states correlations. There exist several corresponding-states correlations which may be used to calculate the second virial coefficients, instead of knowing the full intermolecular potential or experimental second virial coefficients in a large range of temperatures. One of these correlation schemes, developed by Pitzer and Curl [14] for nonpolar fluids and later extended by Schreiber and Pitzer [15] to nonpolar and slightly polar fluids, needs the critical parameters plus the Pitzer acentric factor. The critical constants are not known for many fluids, and the measured values are usually associated with a high degree of uncertainty. Boushehri and Mason [16] proposed a corresponding-states correlation for the second virial coefficient in terms of the latent heat of vaporization, as the temperature reducing constant, and the liquid density at the triple point, as the second virial coefficient reducing constant. Another correlation was developed by Boushehri and Ghatee [17] in terms of the surface tension and the liquid density at the freezing point. These correlations have been used to predict the equation of state of nonpolar fluids [16–18].

Recently, a corresponding-states correlation for the second virial coefficient of nonpolar fluids was developed by Eslami [10], with even less input information (the normal boiling point constants) than the others [14–17]. The correlation has been employed [10] to predict the equation of state of a large number of nonpolar fluids including noble gases, diatomic molecules, saturated hydrocarbons, and a number of aliphatic, aromatic, and cyclic hydrocarbons over a wide range of temperatures and pressures with an accuracy of a few percent. Determination of temperature-dependent parameters of the equation of state by this procedure also self-adjusts the parameter λ to 0.495 [10]. While the present method uses less input information than the others and is easier to apply, it was shown that it has nearly the same [16, 17] predictive power as the previous methods. Our correlation reads

$$B_2\rho_{\text{bp}} = 1.033 - 3.0069\left(\frac{T_{\text{bp}}}{T}\right) - 10.588\left(\frac{T_{\text{bp}}}{T}\right)^2 + 13.096\left(\frac{T_{\text{bp}}}{T}\right)^3 - 9.8968\left(\frac{T_{\text{bp}}}{T}\right)^4 \tag{2}$$

where ρ_{bp} is the liquid density at the normal boiling temperature, T_{bp}. Knowing the second virial coefficient from Eq. (2), the parameters α and b can be calculated by rescaling the empirical formulas in Ref. 13 in terms of normal boiling point constants. The results were shown to be of the form [10]

$$\alpha\rho_{\text{bp}} = a_1\left\{\exp\left[-c_1\left(\frac{T}{T_{\text{bp}}}\right)\right]\right\} + a_2\left\{1 - \exp\left[-c_2\left(\frac{T_{\text{bp}}}{T}\right)^{1/4}\right]\right\} \tag{3}$$

and

$$b\rho_{\text{bp}} = a_1\left[1 - c_1\left(\frac{T}{T_{\text{bp}}}\right)\right]\exp\left[-c_1\left(\frac{T}{T_{\text{bp}}}\right)\right] + a_2\left\{1 - \left[1 + 0.25c_2\left(\frac{T_{\text{bp}}}{T}\right)^{1/4}\right]\exp\left[-c_2\left(\frac{T_{\text{bp}}}{T}\right)^{1/4}\right]\right\} \tag{4}$$

where

$$a_1 = -0.0860, \qquad c_1 = 0.5624$$

$$a_2 = 2.3988, \qquad c_2 = 1.4267$$

Specifying the temperature-dependent parameters in this manner, we have shown [10] that the equation of state can be put in a much simpler form:

$$\frac{p}{\rho kT} = 1 - \frac{(\alpha - B_2)\,\rho}{1 + 0.11b\rho} + \frac{\alpha\rho}{1 - 0.495b\rho} \tag{5}$$

Equation (1) for pure fluids was also extended to mixtures by Ihm, Song, and Mason [6–8]. In the final form, the equation of state for mixtures takes the form [6]

$$\frac{p}{\rho kT} = 1 + \rho\sum_{ij} x_i x_j[(B_2)_{ij} - \alpha_{ij}]\,F_{ij} + \rho\sum_{ij} x_i x_j \alpha_{ij} G_{ij} \tag{6}$$

with

$$F_{ij} = \frac{1}{1-\zeta_3} - \left(\frac{d_i d_j}{d_{ij}}\right) \frac{\frac{1}{6}\pi\rho \sum_k x_k d_k^2 (4\delta_k + 1)}{(1-\zeta_3)(1+\frac{2}{3}\pi\rho \sum_k x_k d_k^3 \delta_k)} \tag{7}$$

$$G_{ij} = \frac{1}{1-\zeta_3} + \left(\frac{d_i d_j}{d_{ij}}\right) \frac{\frac{1}{6}\pi\rho \sum_k x_k d_k^2 (4\lambda_k - 1)}{(1-\zeta_3)(1-\frac{2}{3}\pi\rho \sum_k x_k d_k^3 \lambda_k)} \tag{8}$$

and

$$\zeta_3 \equiv \tfrac{1}{6}\pi\rho \sum_k x_k d_k^3 \tag{9}$$

where x_i and x_j are mole fractions of the components, $\delta_k = 0.22\lambda_k$, G_{ij} is the pair distribution function, and the summation runs over all components of the mixture. The parameters $(B_2)_{ij}$, α_{ij}, and b_{ij} are all related to the intermolecular potential between ij components, and the parameter d_{ij} is related to b_{ij} via the relation

$$b_{ij} = \tfrac{2}{3}\pi d_{ij}^3 \tag{10}$$

The present method for calculating the second virial coefficient and the other two temperature-dependent parameters can be extended to mixtures by using a simple arithmetic mean for the boiling point temperature and a geometric mean for the liquid density at the boiling point; i.e.,

$$(T_{\mathrm{bp}})_{ij} = [(T_{\mathrm{bp}})_i \, (T_{\mathrm{bp}})_j]^{1/2} \tag{11}$$

and

$$(\rho_{\mathrm{bp}})_{ij} = \tfrac{1}{2}[(\rho_{\mathrm{bp}})_i^{-1/3} + (\rho_{\mathrm{bp}})_j^{-1/3}]^{1/3} \tag{12}$$

The purpose of this work is to calculate the temperature-dependent parameters from Eqs. (2)–(4), (11), and (12) and apply the equation of state for the calculation of the liquid density of mixtures with minimum input information.

3. RESULTS AND DISCUSSION

The present correlation for the calculation of the second virial coefficient of mixtures has been used to predict the equation of state of nonpolar fluid mixtures. We have selected several binary and ternary mixtures including mixtures of noble gases, diatomics, and a number of hydrocarbons to check the accuracy of the method. It is known that molar excess volumes are very sensitive to small differences in the values used in their calculations [19]. Therefore, we have chosen molar volume data for comparing the predictive ability of the present formulation with experiment.

The calculated molar volume data for mixtures of Ar–Kr and Kr–Xe are compared with experiment [20, 21] in Fig. 1. Also, the liquid density of quasi-equimolar binary mixtures of Ar–Ne, Ar–Kr, and Ar–Xe at 298.15 K are calculated over a wide range of pressures up to 8000 bar and are compared with experiment [22] in Fig. 2. The calculated ρ–p isotherms for CH_4–CF_4 binary mixtures are shown in Figs. 3 and 4 and are compared with the experimental values of Douslin et al. [23]. Figure 5 shows the calculated compressibility factor isotherms for a ternary mixture of N_2–CH_4–C_2H_6 compared with experiment [24]. The equation of state has also been tested for the prediction of the liquid density of hydrocarbons. The liquid density of cyclo-C_6H_{12}/*n*-C_6H_{14} and that of toluene/*n*-C_8H_{18} binary mixtures, at 1 bar and 298.15 K over the entire concentration range, are compared in Fig. 6 with experimental data [25, 26].

To compare the present method with others, deviation plots for the calculated liquid densities of benzene/*n*-C_6H_{14} and benzene/*n*-C_8H_{18} mixtures, compared with the corresponding-states liquid densities (COSTALD) of Thomson et al. [27], are given in Figs. 7 and 8, respectively. The results for these mixtures are also compared with the previous equations [18, 28], based on correlating second virial data in terms of the heat of vaporization [16] and the surface tension [17]. Furthermore, the present method has been compared with the saturated liquid density correlation of Iglesias-Silva and Hall [29], which has recently been extended to mixtures by Nasrifar et al. [30]. The predicted results from the present scheme and the corresponding-states correlation of Nasrifar et al. [30] for the orthobaric liquid densities of cyclo-C_6H_{12}/*n*-C_6H_{14}, toluene/*n*-C_8H_{18}, C_2H_6–C_3H_8, and R-32/R-134a mixtures are compared with experimental data [25, 26, 31, 32] in Figs. 9 and 10. Although our results are less accurate than the method of Nasrifar et al. [30], their method needs the values of the critical constants, triple-point parameters, acentric factor, an adjustable parameter, and six mixing rules for the mixtures, while our method is easier to apply.

The agreement of the predicted results with experimental data in all cases is within ±5%. Unlike most conformal solution theories, this equation of state does not seem to deteriorate when the size and energy parameters of components are varied. The equation of state is simple in form and easy for practical applications. The parameters can be obtained from knowing just the normal boiling point constants. The procedure, outlined here, shows that *pvT* properties of nonpolar fluid mixtures can be obtained with reasonable accuracy from just two scaling constants, T_{bp} and ρ_{bp}, without knowing any details of the intermolecular forces. However, since

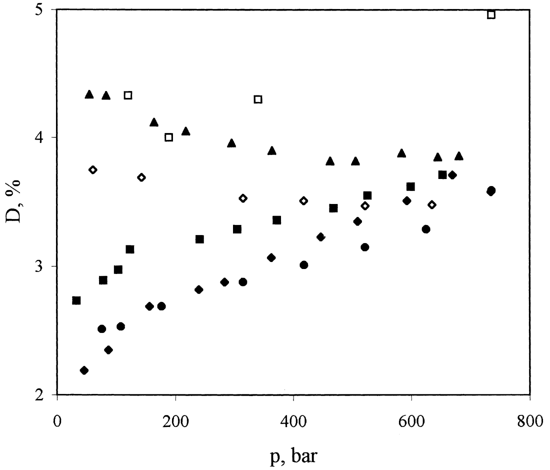

Fig. 1. Deviation plot for the density of Ar–Kr mixtures at 134.32 K [20] and Kr–Xe mixtures at 190.01 K [21] vs pressure. 0.277Ar+0.723Kr (◆), 0.485Ar+0.515Kr (■), 0.689Ar+0.302Kr (▲), 0.319Kr+0.681Xe (●), 0.556Kr+0.444Xe (◇), and 0.707Kr+0.293Xe (□).

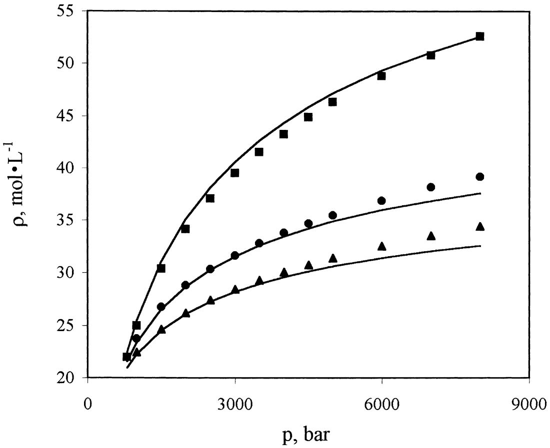

Fig. 2. Molar density of 0.499Ar+0.501Ne (■), 0.5095Ar+0.4905Kr (●), and 0.5016Ar+0.4984Xe (▲) vs pressure at 298.15 K. The curves represent our calculated values, and the symbols are experimental values [22].

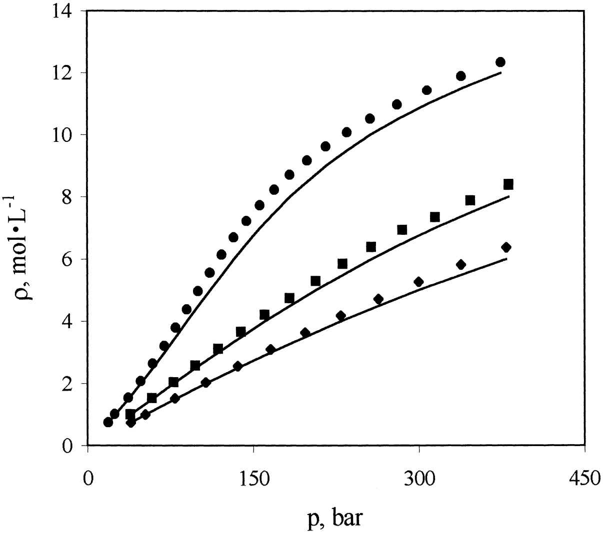

Fig. 3. Molar density of $0.25CH_4 + 0.75CF_4$ versus pressure at 323.15 K (●), 473.15 K (■), and 623.15 K (◆). The curves are from the present equation of state, and the symbols are the experimental values [23].

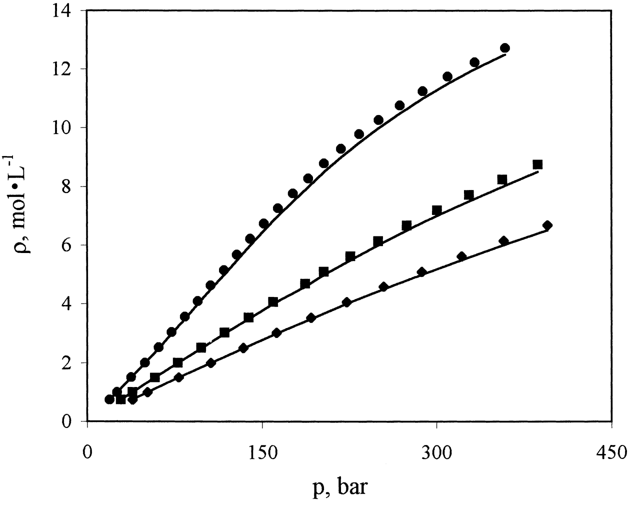

Fig. 4. Same as Fig. 3 for $0.75CH_4 + 0.25CF_4$.

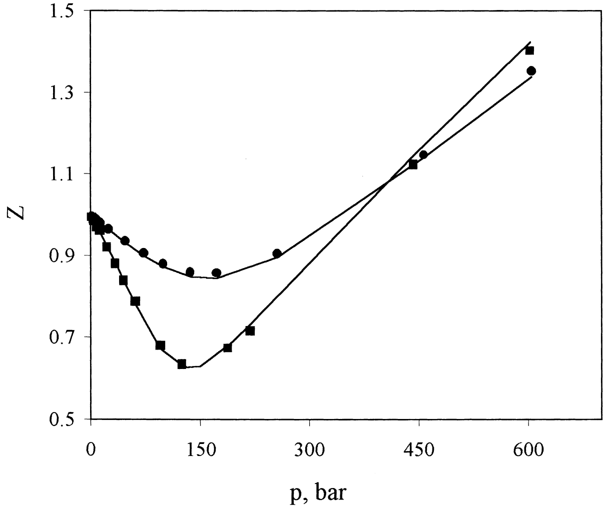

Fig. 5. Compressibility factor vs pressure for $0.1209N_2 + 0.6265CH_4 + 0.2526C_2H_6$ at 275 K (■) and 345 K (●). The curves are from this work, and the symbols represent the experimental values [24].

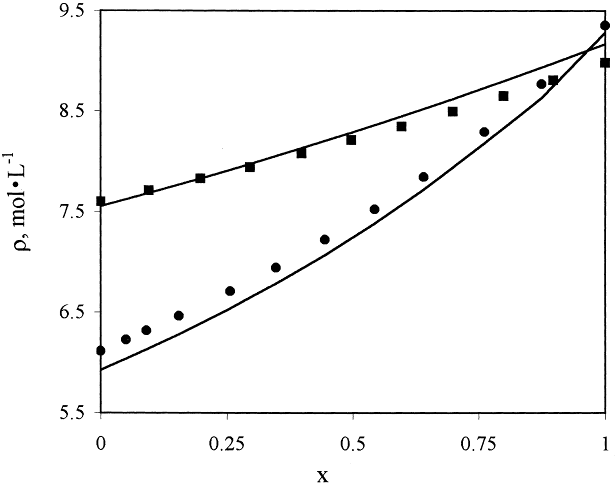

Fig. 6. Molar density for binary mixtures of x[cyclo-C_6H_{12}]+$(1-x)$[n-C_6H_{14}] (■) and x[C_7H_8]+$(1-x)$[n-C_8H_{18}] (●) at 1 bar and 298.15 K. The curves and symbols represent the results from the present equation of state and from experiment [25, 26], respectively.

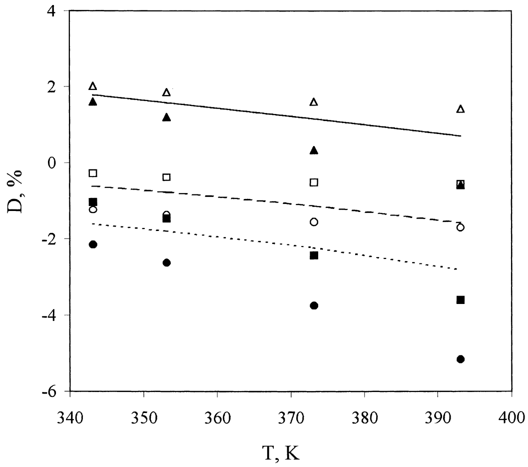

Fig. 7. Deviation plots for the calculated molar density of $0.5C_6H_6 + 0.5n\text{-}C_6H_{14}$ compared with the COSTALD method [27]. The filled symbols show the calculated values from Ref. 28 at 15 bar (●), 100 bar (■), and 400 bar (▲) while the corresponding open symbols are from Ref. 18. The curves represent our predicted values at 15 bar (···), 100 bar (– –), and 400 bar (—).

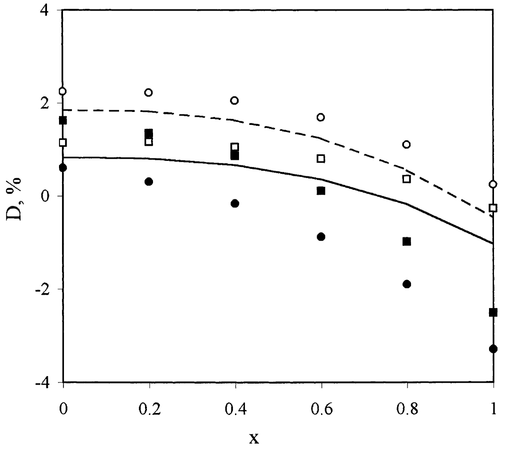

Fig. 8. Deviation plots for $x[C_6H_6] + (1-x)[n\text{-}C_8H_{18}]$ mixtures at 373.15 K compared with the COSTALD method [27]. The filled symbols show the calculated values from Ref. 28 at 15 bar (●) and 100 bar (■), and the corresponding open symbols are from Ref. 18. The curves represent our predicted values at 15 bar (—) and 100 bar (– –).

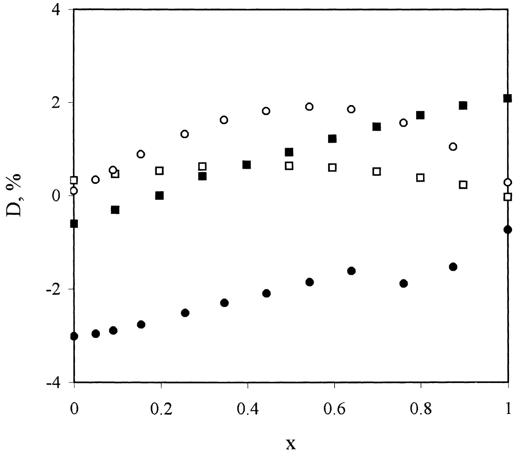

Fig. 9. Deviation plot for the density of x[cyclo-C_6H_{12}] + $(1-x)$[n-C_6H_{14}] (■) and x[C_7H_8] + $(1-x)$[n-C_8H_{18}] (●) at 1 bar and 298.15 K compared with experiment [25, 26]. The filled and open symbols represent our calculations and the results from corresponding-states correlation of Nasrifar et al. [30], respectively.

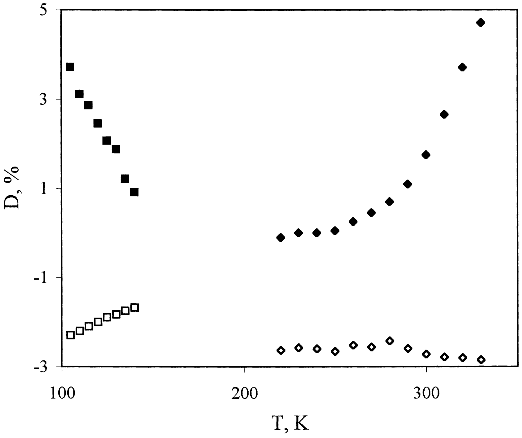

Fig. 10. Deviation plot for the orthobaric liquid density of $0.5015C_2H_6 + 0.4985C_3H_8$ (■) and 0.3955R-32 + 0.6045R-134a (◆) compared with experiment [31, 32]. The filled and open symbols represent our calculations and the results from corresponding-states correlation of Nasrifar et al. [30], respectively.

the underlying theory is based on a mean-field approximation, it is not accurate in the two-phase and critical regions. Therefore, we do not recommend the present scheme for the calculation of vapor pressures or critical constants.

Although the compounds studied in this work have a variety of complexities, and hence different intermolecular forces, Eqs. (3) and (4) for α and b, respectively, which have been obtained [13] using the results for a simple Lennard–Jones potential, can still well reproduce the experimental data. The reason is that the parameters α and b depend only on the repulsive branch of the potential energy function and are insensitive to the details of the intermolecular forces [5].

Finally, the present method does not need the critical parameters, which are scarce for many substances and are subject to higher experimental uncertainties than those of the normal boiling point parameters. Also, it does not need such properties as the heat of vaporization [16] or surface tension [17]. Furthermore, the present equation of state is simpler than the others [16–18, 28] in that the parameters λ_i are all equal and set to 0.495. Comparison of our calculated results in Figs. 7–10 with those obtained by the previous methods [18, 28, 30] reveals that the present scheme is a satisfactory method for *pvT* data prediction of mixtures.

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