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Thermophysical Property Predictions from the Software Package EOSMIX[1]

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A two-fluid corresponding-states model for predicting the thermodynamic properties of mixtures has been developed, which uses accurate equations of state for the reference substances of the components. A new mixing parameter has been introduced, which takes account of the differences in molecular sizes in binary fluid mixtures. The three mixing parameters for methane–ethane and methane–propane have been optimized using different types of experimental data. Comparisons of predictions with data are given for experimental densities and speed of sound.

KEY WORDS: corresponding states; methane–ethane; methane–propane; mixing rules; mixture predictions; two-fluid model; thermodynamic properties.

1. INTRODUCTION

Models based on the principle of corresponding states have been used extensively in recent years for predicting the equilibrium thermodynamic properties of mixtures. The most frequently used form is that of the van der Waals "one-fluid" approximation, where the residual Helmholtz energy of the mixture is approximated by that of a hypothetical pure equivalent substance. The quality of the predictions is then dependent on the choice of the reference substance as well as on the expressions for the scaling parameters. In principle, the reference substance need not be the same for all conditions, but any changes within a given mixture would lead to discontinuities in the derived thermodynamic properties. However, using a single reference substance may lead to variations in the quality of the predictions, depending

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on the composition. For example, using an equation of state (EOS) for N_2 to predict the properties of a N_2–CO_2 mixture will give good results for the N_2-rich mixture but these will be less accurate for the CO_2-rich end, whereas a CO_2 EOS will give the reverse [1].

We have developed, over the last 10 years, a computer software package, EOSPAC, which now contains accurate equations of state for 19 pure fluids, of which 12 have been internationally validated. These are now being used as the basis for the development of a new package, called EOSMIX, for calculating equilibrium thermodynamic properties of multicomponent systems. The two-fluid corresponding-states model (VDW2) is used, in which each component of the mixture is represented by a hypothetical substance and these are then mixed ideally. The properties of each hypothetical substance can be related by the principle of corresponding states, to those of any real pure fluid. Predictions using EOSMIX for air are given in Ref. 2, and those for CO_2–H_2O and N_2–H_2O mixtures in Refs. 2 and 3.

2. THEORY

In this work the VDW2 model based on that described by Rowlinson and Watson [4] is used where the real fluid mixture is assumed to consist of an ideal mixture of hypothetical components. The residual Helmholtz energy of the mixture is then given by

$$A_{\mathrm{mix}}^{\mathrm{res}}(V, T, x) = \sum_i x_i A_i^{\mathrm{res}}(V, T) \tag{1}$$

where x_i is the mole fraction of component i, $A_i^{\mathrm{res}}(V, T)$ is the residual Helmholtz energy of the ith hypothetical component, and V and T are the mixture volume and temperature. Following the principle of corresponding states, the residual Helmholtz energy of each hypothetical component can, in turn, be expressed in terms of a real reference substance r_i so that

$$A_i^{\mathrm{res}}(V, T) = f_i A_{r_i}^{\mathrm{res}}(V/h_i, T/f_i) \tag{2}$$

where f_i and h_i are the scaling parameters of hypothetical component i with respect to its reference substance r_i. For the VDW2 model these are given by

$$h_i = \sum_j x_j h_{ij} \tag{3}$$

$$f_i h_i = \sum_j x_j h_{ij} f_{ij} \tag{4}$$

with the Lorenz–Berthelot combining rules used to determine the cross parameters h_{ij} and f_{ij}:

$$h_{ij} = \eta_{ij}\left[\frac{h_{ii}^{1/3} + h_{jj}^{1/3}}{2}\right]^{3} \tag{5}$$

$$f_{ij} = \xi_{ij}(f_{ii}f_{jj})^{1/2}. \tag{6}$$

The binary-interaction parameters for components i and j, η_{ij} and ξ_{ij}, are adjustable but will have fixed values for each component pair in the mixture. The terms h_{ii} and f_{ii} are calculated from

$$h_{ii} = (V_i^c/V_{r_i}^c)\,\phi(V_i^R, T_i^R) \tag{7}$$

$$f_{ii} = (T_i^c/T_{r_i}^c)\,\theta(V_i^R, T_i^R) \tag{8}$$

with a similar pair of equations for h_{jj} and f_{jj}. V_i^c and T_i^c are the critical volume and critical temperature of component i, respectively, and $V_{r_i}^c$ and $T_{r_i}^c$, are the critical properties of reference fluid r_i. ϕ and θ are called molecular shape factors. "Universal" shape-factor correlations for the alkanes as functions of reduced temperature, reduced volume, critical compression factor, and the Pitzer acentric factor were given by Leach et al. [5] and are used in this work. Finally, the arguments of ϕ and θ are given by

$$V_i^R = \phi V/(V_{r_i}^c h_i) \tag{9}$$

$$T_i^R = \theta T/(T_{r_i}^c f_i) \tag{10}$$

For each component in Eq. (1) a pair of scaling parameters is required for Eq. (2) and these are calculated from Eqs. (3)–(10) with an appropriate reference EOS.

This form of VDW2 model predicts accurate values for mixtures when the molecules of the different components are of similar size, but the predictions deteriorate progressively as the size difference grows. To improve the accuracy of the predictions for molecules of different sizes, the mixing rules were modified by introducing a third adjustable parameter, λ_{ij} [6]. Equations (3) and (4) now read

$$h_i = \sum_j x_j h_{ij}\zeta_{ij} \tag{11}$$

$$f_i h_i = \sum_j x_j h_{ij} f_{ij}\zeta_{ij} \tag{12}$$

$$\zeta_{ij} = \frac{2h_{ij}^{\lambda_{ij}/3}}{h_{ii}^{\lambda_{ij}/3} + h_{jj}^{\lambda_{ij}/3}} \tag{13}$$

The original VDW2 model is retrieved when $\lambda_{ij}=0$. This new model, which uses a modification of the Lebowitz solution of the Percus–Yevick approximation, is called the MLPY model. The Lorenz–Berthelot combining rules for the cross parameters h_{ij} and f_{ij}, as given in Eqs. (5) and (6), are retained. The three adjustable binary interaction parameters, η_{ij} and ξ_{ij}, as before, and λ_{ij}, were optimized using accurate binary mixture data with λ_{ij} varying between 0 and 2. Derivation of the MLPY model is given by Cha [6].

3. RESULTS

Two of the most important mixtures for predicting the properties of natural gas and liquefied natural gas (LNG) are those of methane–ethane and methane–propane. Data for these, in the natural gas region, have recently been critically reviewed by the Groupe Européen de Recherches Gazières (GERG) and are listed in their data bank [7]. The results discussed below are for the prediction of single-phase properties only.

3.1. Methane–Ethane Mixtures

The reference EOS used for the mixture components were the methane equation of Setzmann and Wagner [8] for methane and the ethane equation of Friend et al. [9] for ethane. The data of Haynes et al. [10] cover a wide range, extending well into the liquid phase, so these, together with the gas-phase speed-of-sound data of Trusler [11], were used to determine the optimum values of the binary-interaction parameters η_{ij} and ξ_{ij} and the MLPY parameter λ_{ij}; these are listed in Table I. The nonlinear-optimization program by Watson [12], based on an algorithm by Powell [13], was used to minimize the sum-of-squares of the density and speed-of-sound deviations of the selected data.

Comparisons of predictions along representative isochores with the experimental densities of Haynes et al. are shown in Fig. 1. Over the whole temperature, pressure, and composition range, the average absolute deviation is 0.56%, with only 25 of the 414 data points deviating by more than 1%. This includes the five points on the 3.9 mol dm^{-3} isochore, which

Table I. Optimum Values for η_{ij}, ξ_{ij}, and λ_{ij}

System	η_{ij}	ξ_{ij}	λ_{ij}
Methane–ethane	1.00724	0.999584	0.812283
Methane–propane	1.03640	0.985498	0.939363

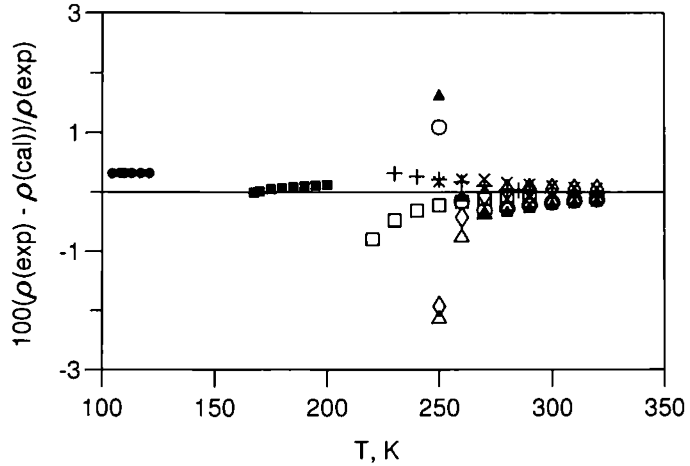

Fig. 1. Selected comparisons of predicted densities ρ(cal) from the MLPY model for methane–ethane mixtures with values ρ(exp) from Haynes et al. [10] for $x_{CH_4} = 0.68526$. Isochores in mol dm^{-3}: (+) 1.0; (×) 3.6; (◇) 5.9; (△) 7.8; (▲) 10.6; (○) 11.6; (□) 15.6; (■) 21.0; (●) 25.3.

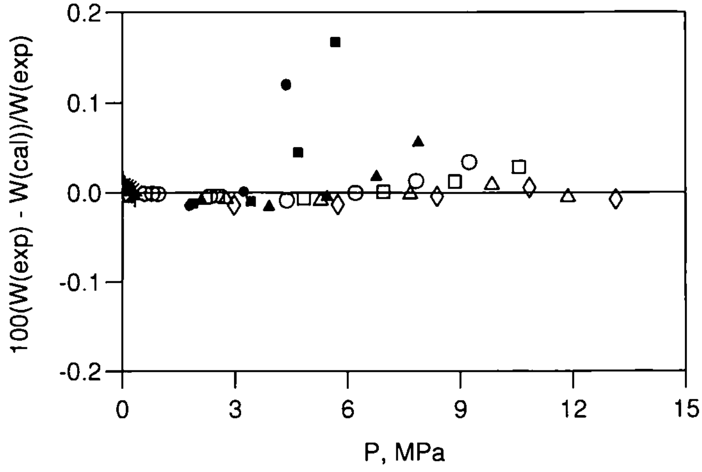

Fig. 2. Comparison of predicted speeds of sound W(cal) from the MLPY model for methane–ethane mixtures with values W(exp) from Trusler [11] for $x_{CH_4} = 0.802$. Isotherms: (+) 200 K; (×) 225 K; (●) 240 K; (■) 250 K; (▲) 275 K; (○) 300 K; (□) 325 K; (△) 350 K; (◇) 375 K.

deviate systematically by more than 10%: These values were not used to optimize the parameters. Our overall predictions compare very favorably with the one-fluid model of Friend and Ely [14], who report an average absolute deviation of 0.77% for the same data. Both models display regions of the *PVTx* surface where the predictions are significantly worse than the average and these are close to the phase boundary and near to the critical line of the mixture.

The Ruhrgas data from the GERG data bank [7] were not used in the optimization of the parameters but their densities agree with the predicted values to within ±0.1%, except for mixtures with the lowest methane concentration, between 270 and 280 K, where the difference increases to about 0.16% near 12 MPa. These deviations are slightly greater than those calculated from the GERG equation which had been fitted to their selected data.

Predictions of the speed-of-sound agree with the data of Trusler [11] mostly within ±0.05%, with almost-uniform scatter about the zero line as shown in Fig. 2. The largest deviations occur along the 240 K isotherm near the saturation boundary, where they reach 0.74% (not shown). Trusler [11] shows that deviations of his data from predictions with the AGA8-92 equation of state [15] are systematic, ranging from −0.1% at 375 K and 13 MPa to 0.8% at 240 K and 6 MPa.

3.2. Methane–Propane Mixtures

The reference EOS used for methane was the methane equation of Setzmann and Wagner [8], and that for propane was the EOS for propane of Bühner et al. [16]. The methane–propane system has not been studied as thoroughly as the methane–ethane one. Two early sets of data by Reamer et al. [17] and Huang et al. [18] cover a wide range of *P*, *T*, and composition. The most recent measurements are those in the GERG [7] data bank, which cover the natural gas region. Recently Trusler et al. [19] have measured the speed of sound in the gas phase of mixtures containing 85 mol% methane over the range 280–375 K for pressures between 0.2 and 13.0 MPa.

A selection of 618 *PVTx* data points from GERG [7], Huang et al. [18], and Reamer et al. [17], together with the 30 measurements of the speed of sound by Trusler et al. [19], was used to find the optimum values of η_{ij}, ξ_{ij}, and λ_{ij}, as described for the methane–ethane system, and their values are listed in Table I. Deviations between the Huang et al. densities and the predictions are mostly within ±1.0%, while those for Reamer et al. are mostly within ±2.0% with 41 of their 1516 data points lying outside this range. Figure 3 shows typical density comparisons for the Reamer

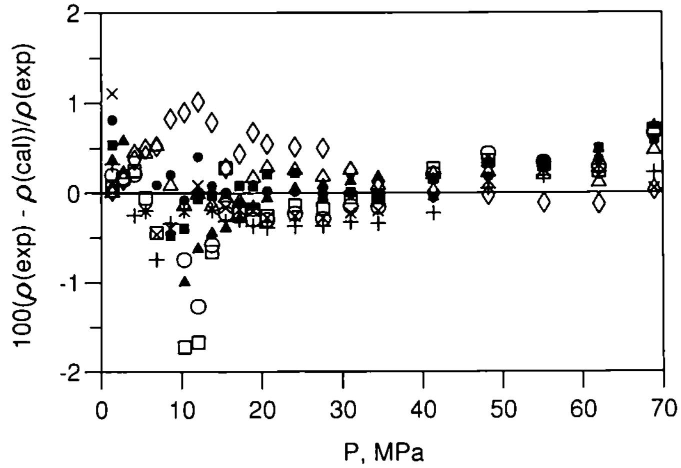

Fig. 3. Selected comparisons of predicted densities ρ(cal) from the MLPY model for methane–propane mixtures with values ρ(exp) from Reamer et al. [17] at 311 K. x_{CH_4} = (+) 0.1, (×) 0.2, (●) 0.3, (■) 0.4, (▲) 0.5, (○) 0.6, (□) 0.7, (△) 0.8, and (◇) 0.9.

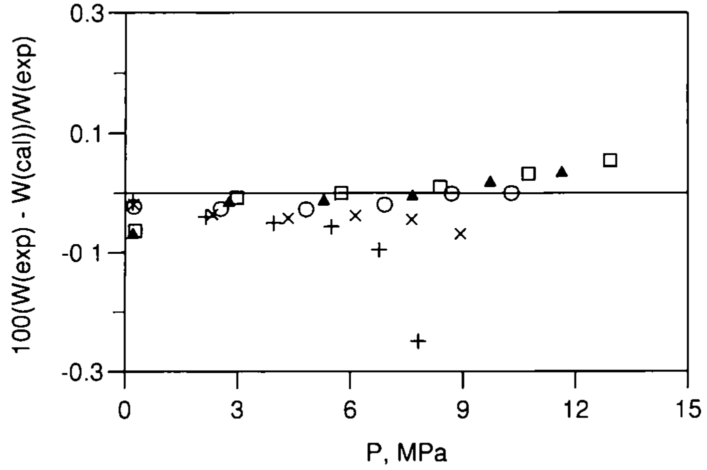

Fig. 4. Comparison of predicted speeds of sound W(cal) from the MLPY model for methane–propane mixtures with values W(exp) from Trusler et al. [19] for x_{CH_4} = 0.849. Isotherms: (+) 280 K; (×) 300 K; (○) 325 K; (▲) 350 K; (□) 375 K.

et al. data at 311 K over the whole composition range. Comparisons of the GERG densities with predictions show all but 16 of their 217 data points agreeing within ±0.05%.

Comparisons with the speed-of-sound data of Trusler et al. [19] are shown in Fig. 4. Except for a single point, agreement with prediction is within ±0.1%. There is a slight negative offset in the deviations below 9 MPa, increasing up to −0.07% at zero pressure, which suggests some inconsistency between the ideal gas values of Trusler et al. [19] and those used by EOSMIX. Above 9 MPa, the deviations diverge positively to reach a maximum value around 0.06% at the maximum pressure. These results compare very favorably with those obtained from the AGA8-85 equation [20], where deviations of 0.5% were recorded at the highest pressures.

4. CONCLUSIONS

This study and the earlier work of Cha et al. [1] on VLE systems have shown that the two-fluid corresponding-states model can give good predictions for the thermodynamic properties of mixtures. Use of a third adjustable parameter, λ_{ij}, improves the predictions of properties over most of the fluid surface. The model is dependent on the a priori existence of suitable accurate equations of state for the reference fluids and work is in progress to enlarge the pure fluid equation-of-state bank in EOSMIX to include all available accurate EOS.

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