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Vapor–Liquid Equilibria of Binary Mixtures of Alkanols with Alkanes from Atmospheric Pressure to the Critical Point[1]

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A reformulated version of the Wong–Sandler mixing rule and the Peng–Robinson equation of state are used for the correlation and prediction of the vapor–liquid equilibrium of several alkanol + alkane binary systems. The description of these mixtures provides a stringent test since cubic equations of state with conventional mixing rules usually predict false liquid–liquid splits for such systems. For all systems, the model parameters used were fit to data on the lowest-temperature isotherm and then higher-temperature isotherms were successfully predicted with those parameters. False phase splitting was avoided by using a constrained parameter fit. For highly asymmetric (in size) alkanol + alkane binaries four parameters were necessary for an accurate representation of the data, while for less asymmetric alkanol + alkane binaries only two parameters were used.

KEY WORDS: alkane; alkanol; mixing rules; vapor–liquid equilibrium.

1. INTRODUCTION

The correlation and/or prediction of phase equilibrium of complex mixtures over broad ranges of temperature and pressure is an important problem in chemical process design. In many cases, especially process simulation, cubic equations of state are preferred for such computations. For these equations to be successful, they must accurately predict saturation pressures of pure

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substances, and effective mixing rules must be available for their use with multicomponent mixtures.

Recently the Wong–Sandler (WS) mixing rule has been introduced to describe highly nonideal mixtures [1] and various implementations have been considered [2–4]. In these studies it was shown that this mixing rule, coupled with a proper two-parameter cubic equation of state, has a broad range of applicability; it can be used as a multiparameter correlative model to fit accurately phase equilibrium data of highly nonideal mixtures [1], or it can be used as a predictive model [2, 3] with parameters obtained from excess Gibbs free energy information. A recently reformulated, two-parameter form of the Wong–Sandler mixing rule allows complete compatibility of this mixing rule with the traditional van der Waals one-fluid mixing rule [4].

In this work, as a part of a program in which applications of WS rule to various complex mixtures of industrial importance are investigated, we explore the capabilities of this mixing rule for the correlation and prediction of binary vapor–liquid equilibrium of alkanols with alkanes. Alkanol + alkane mixtures are important in a number of industrial applications including oxygenated gasolines. Also, light hydrocarbon (methane, ethane) and alcohol mixtures are encountered in the production of C_1 to C_6 alcohols from syngas, and n-alkanes may be used as a dehydrating entrainer in the azeotropic distillation of alcohols as a replacement for cyclic hydrocarbons.

While there are considerable data for alkanol + alkane systems, in engineering applications it is usually necessary to extrapolate or interpolate available data to the pressure and temperature of interest. In some cases one of the components of the mixture may be supercritical, adding to the complexity of the phase behavior. Alkanol + alkane systems have also been rather difficult to describe with cubic equations of state. Frequently, especially at low temperatures, a liquid-liquid split is predicted by equation of state models, which is not found in the experimental data [5–8].

2. THE MODEL

The basic relations of the Wong–Sandler mixing rule for the equation of state parameters a_{m} and b_{m} are

$$b_{\mathrm{m}} - \frac{a_{\mathrm{m}}}{RT} = \sum_i \sum_j x_i x_j \left(b - \frac{a}{RT}\right)_{ij} \tag{1}$$

$$\frac{A_x^{\mathrm{E}}}{C} = \frac{a_{\mathrm{m}}}{b_{\mathrm{m}}} - \sum_i x_i \frac{a_i}{b_i} \tag{2}$$

where A^E is a Helmholtz excess free energy term, a and b are equation of state parameters, R is the gas constant, T is the absolute temperature, and C is a constant dependent on the equation of state selected; $C = (1/\sqrt{2})\ln(\sqrt{2}-1)$ for the modified Peng–Robinson [9] equation used here. For the excess Helmholtz free energy model, a modified nonrandom two-fluid (NRTL) expression [4] was used,

$$\frac{A^E}{RT} = \sum_i x_i \left[\frac{\sum_j x_j G_{ji} \tau_{ji}}{\sum_k x_k G_{ki}}\right] \tag{3}$$

with

$$G_{ji} = b_j \exp(-\alpha_{ij} \tau_{ji}) \tag{4}$$

In this work, the following relation was used for the cross coefficient,

$$\left(b - \frac{a}{RT}\right)_{ij} = \frac{(b_i + b_j)}{2} - \frac{\sqrt{a_i a_j}(1 - k_{ij})}{RT} \tag{5}$$

Equations (3) to (5) are from a recent formulation of the WS rule [4] that allows this mixing rule to reduce to the conventional van der Waals mixing rule whenever required merely by a choice of one of its parameters (i.e., $\alpha_{ij} = 0$).

The model parameters here are k_{ij} in Eq. (5) and α_{ij}, τ_{ij}, and τ_{ji} in Eq. (4). Our approach in this work is to correlate, using all four parameters if necessary, data for the lowest temperature isotherm for the systems considered and then to predict the vapor–liquid equilibria at higher temperatures with those parameters. The reason for this strategy is that the problem here is not the lack of data for the systems considered, rather, it is the lack of data in desired ranges of temperature and pressure. Thus we examine how low-temperature/low-pressure data, correlation of which by means of an equation of state has heretofore been difficult, can be used to develop a model to predict phase behavior at high temperatures and pressures.

3. ALKANOL + ALKANE SYSTEMS

The systems investigated are methane + ethanol and ethane + ethanol [10] from 298 to 498 K, propane + methanol [11] from 313 to 373 K, butane + ethanol [12] from 298.3 to 345.7 K, and pentane + methanol [13] and pentane + ethanol [14] from 373 to 423 K.

For all these systems the lowest-temperature isotherm was fit using all four parameters. The remainder of the data were then compared with the

Table I. Model Parameters Used in This Work

System	α	k_{12}	τ_{12}	τ_{21}
Methane + ethanol	0.900	0.000	0.5562	0.8000
Ethane + ethanol				
Fitted to 348 K	0.500	0.101	6.5000	1.2500
Fitted to 298 K	0.560	0.093	6.3400	1.2300
Propane + methanol	0.532	0.300	5.4100	1.7200
Butane + ethanol	0.650	0.342	3.8000	0.8500
Pentane + methanol				
Four-parameter fit	0.500	0.311	3.9514	1.7172
Two-parameter fit	0.100	0.000	7.0802	−4.500
Pentane + ethanol				
Four-parameter fit	0.500	0.201	2.8946	0.7544
Two-parameter fit	0.100	0.000	6.1735	−3.299

model predictions. Only total pressure was used in the objective function, and a simple minimization routine was used. A common problem with multiparameter data fitting is that there may be more than one set of parameters that fit the data with comparable accuracy. Thus the first task is to make reasonable a priori estimates for the parameters. Our previous studies with hydrogen + hydrocarbon binaries [15] indicate that for very asymmetric binary mixtures, a relatively large value of α, perhaps close to unity, may be necessary. Also, $k_{ij} = 0$ was used as the initial guess. A recent study by Eubank [16] suggests that this parameter can be computed directly from the second virial cross coefficients of a gas mixture, however, we have treated k_{ij} as an adjustable parameter. For the modified NRTL model parameters, $\tau_{12} = \tau_{21} = 1$ were used as initial guesses. Occasionally these selections did not lead to convergence: In such cases other initial guesses were tried. The values of the optimized parameters found here are reported in Table I.

The results for methane + ethanol system are presented in Fig. 1. For this system methane is supercritical at all temperatures investigated, and false liquid–liquid splitting was not encountered. We see that very good predictions are possible even at 498 K with the parameters obtained based on data at 299 K, except that gas phase compositions are predicted to be slightly too lean in methane.

Results for the ethane + ethanol mixture are reported in Fig. 2. At the lowest temperature (298 K) ethane is subcritical, and when this isotherm was fit it was found that the parameters that resulted in the best fit of the pressure data led to a false liquid–liquid phase split. Consequently,

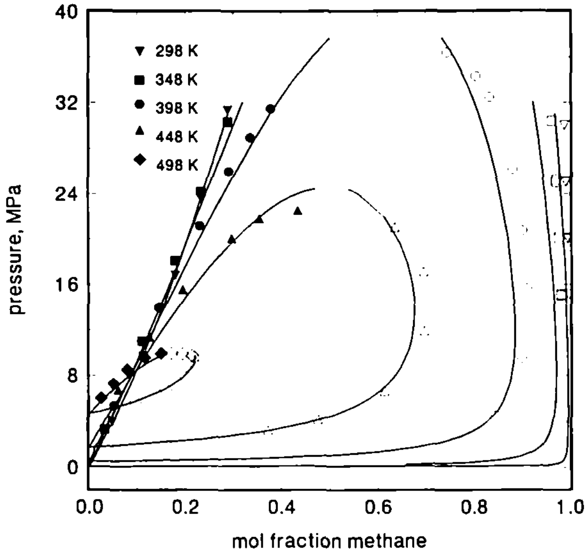

Fig. 1. Vapor–liquid equilibrium for the methane–ethanol system.

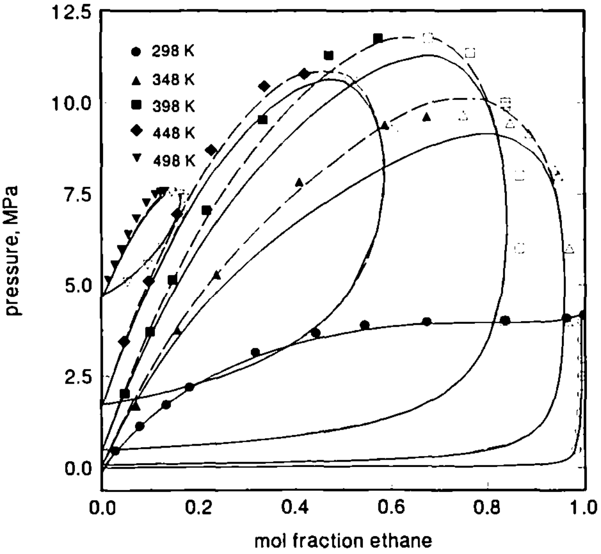

Fig. 2. Vapor–liquid equilibrium for the ethane–ethanol system. Solid line, parameters fit to model parameters fit to 298 K data; dashed lines, model parameters fit to 348 K data.

following the suggestion of Englezos et al. [6], a constrained parameter fit was performed at 298 K. When the isotherms are predicted with the parameters obtained this way (solid lines in Fig. 2), it is observed that while the general phase behavior is captured, pressure predictions are systematically lower than the experimental measurements. We then used the second lowest isotherm (348 K) to refit the parameters and estimated phase equilibrium with these parameters up to 498 K. These results, represented in Fig. 2 as dashed lines, are significantly better.

The results for the propane + methanol mixture are presented in Fig. 3. This system was studied earlier in detail by Schwartzentruber et al. [5] and, with their mixing rule, was found to exhibit a false liquid split. Therefore a constrained parameter fit was used to fit 313 K data, and then other isotherms were predicted with good accuracy with the same parameters. With slight changes in the parameters, excellent fits of the 343 and 373 K isotherms are possible, though this is not reported here.

Figure 4 shows the results obtained for a butane + ethanol binary mixture. This system exhibited a false liquid–liquid split at 298.3 K with parameters obtained with an unconstrained regression, but to a much smaller extent than mixtures of ethane or propane with ethanol. With the best parameters obtained from a constrained fit, we see that it is possible to represent all three isotherms very accurately.

A general characteristic we have observed for mixtures of light hydrocarbons (C_4 and lighter) with alcohols is that a large α value and a nonzero k_{ij} value were required for a good fit of the experimental data. On the other hand, for the heavy hydrocarbon (C_5 and heavier) + alcohol systems, it was possible to obtain good fits of the experimental data with parameter sets of widely varying values. This point is considered below.

The results for pentane + methanol mixture are presented in Fig. 5. Here the solid lines are obtained with the parameter set 0.5/0.31/3.95/1.72 for α, k_{ij}, τ_{ij}, and τ_{ji}, respectively, all fitted to the 373 K data. The dashed lines are obtained by fixing $\alpha = 0.1$ and $k_{ij} = 0$ and fitting only two parameters to the 373 K data to obtain $\tau_{12} = 7.08$ and $\tau_{21} = -4.50$ following suggestions given elsewhere [4]. The parameter values for these two cases are quite different, and it is also possible to obtain other sets of parameters of varying accuracy between these two. While the four-parameter fit gives a better description of the 373 K isotherm, especially at the two ends of the composition range, the two-parameter fit also describes the phase behavior with reasonable accuracy; moreover, the two-parameter model predicts the 423 K isotherm slightly more accurately than the four-parameter model.

Similar behavior was obtained for the pentane–ethanol mixture, as shown in Fig. 6, though with less difference between the four- and two-parameter models. Here the solid lines were obtained with the four-parameter

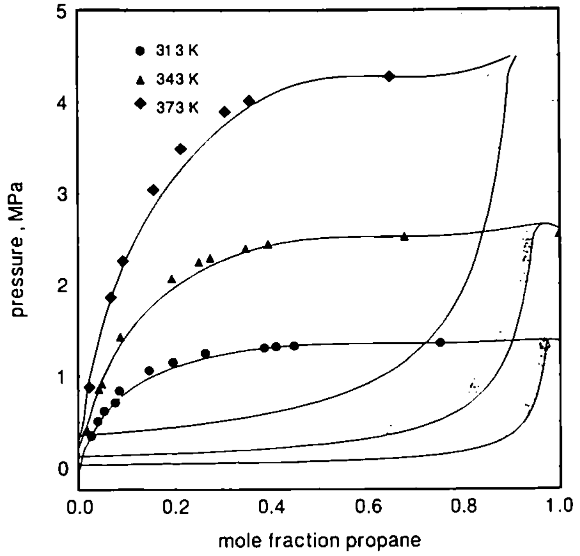

Fig. 3. Vapor-liquid equilibrium for the propane-methanol system.

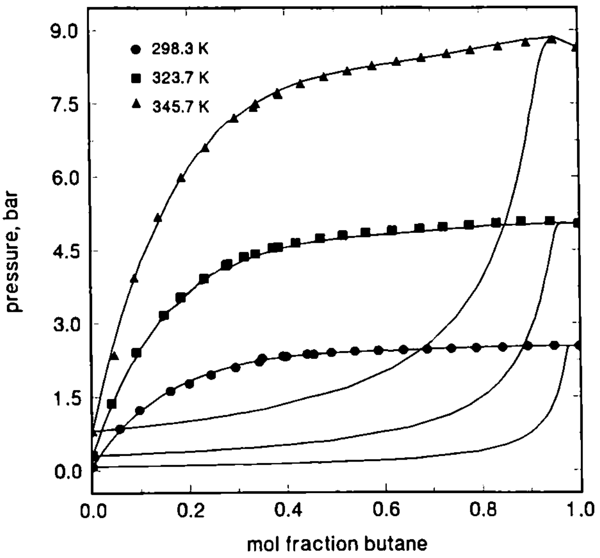

Fig. 4. Vapor liquid equilibrium for the butane ethanol system.

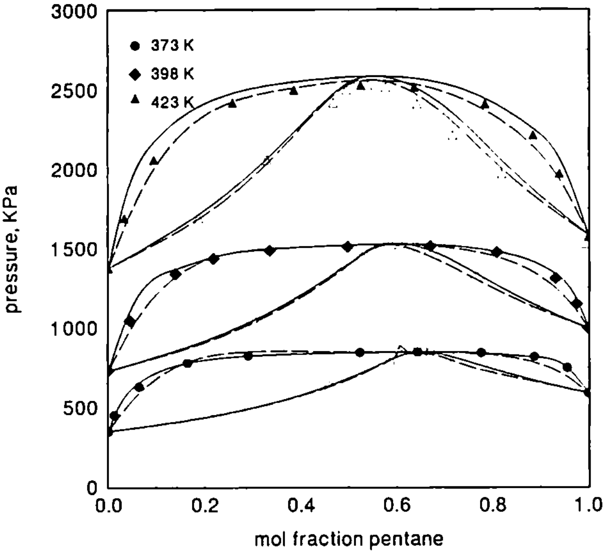

Fig. 5. Vapor–liquid equilibrium for the pentane–methanol system. Solid lines, four parameters fit to 373 K data; dashed lines, two parameters fit to 373 K data.

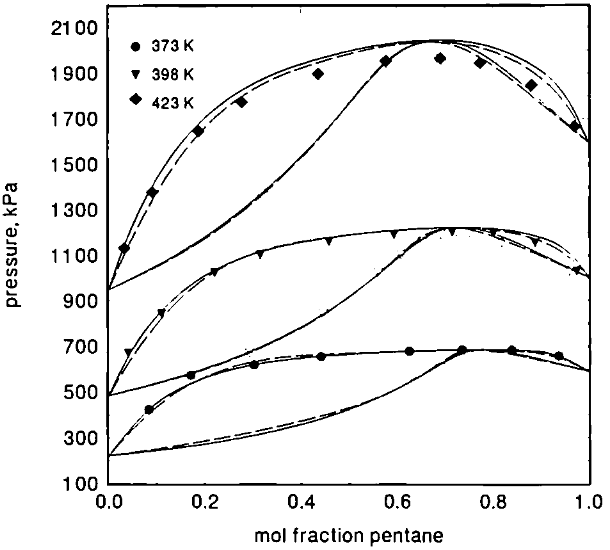

Fig. 6. Vapor–liquid equilibrium for the pentane–ethanol system. Solid lines, four parameters fit to 373 K data; dashed lines, two parameters fit to 373 K data.

set 0.5/0.2/2.9/0.75, and the dashed lines with the two-parameter set 0.1/0.0/6.17/−3.30 for α, k_{12}, τ_{12}, and τ_{21}, respectively. One conclusion is that for mixtures which are not very asymmetric in size, the model is not very sensitive to a particular parameter choice, as a change in the value of one model parameter can be easily compensated by varying the value of another parameter. This may explain the large numerical values of the NRTL parameters for the two-parameter case considered above.

4. CONCLUSIONS

In this work the capabilities of the WS mixing rule for extrapolating available low-temperature data to higher temperatures and pressures has been studied for a number of alkane + alkanol binary systems. It is shown that the WS mixing rule can be used successfully to correlate low-temperature data of asymmetric light hydrocarbon + alkanol systems. These are the systems for which many conventional equation of state models fail by predicting false liquid phase splits. In addition, it is shown that for these cases one set of parameters correlated using data from a low-temperature isotherm can yield quite accurate predictions of the phase behavior at temperatures up to 200 K higher. However, all four parameters of the new mixing rule are necessary for a good fit in these cases.

Examining the optimized parameters for the various systems suggests that with the exception of methane + alkanol mixture, a reasonable value for α is from 0.5 to 0.6, and if a value of k_{12} can be obtained from second virial coefficient data as suggested by Eubank [16], then the mixing rule can be used as a two-parameter model.

For mixtures of alkanols with hydrocarbons heavier than C_4, it was found that a variety of values may be found for the mixing-rule parameters that give comparable and quite acceptable correlations and/or predictions. Consequently, if enough data are available, these may be used to correlate the four model parameters. In the absence of a sufficient amount of data, the two-parameter predictive method introduced recently [4] has been shown to be very useful for estimating the high-temperature behavior of such systems from low-temperature information.

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REFERENCES

1. D. S. H. Wong and S. I. Sandler, *AIChE J.* **38**:671 (1992).
2. D. S. H. Wong, H. Orbey, and S. I. Sandler, *Ind. Eng. Chem. Res.* **31**:2033 (1992).
3. H. Orbey, D. S. H. Wong, and S. I. Sandler, *Fluid Phase Equil.* **85**:4 (1993).
4. H. Orbey and S. I. Sandler, *AIChE J.* **41**:683 (1995).
5. J. Schwartzentruber, F. Galivel-Solastiouk, and H. Renon, *Fluid Phase Equil.* **38**:217 (1987).
6. P. Englezos, N. Kaogaris, and P. R. Bishnoi, *Fluid Phase Equil.* **53**:81 (1989).
7. M. R. Margerum and B. C.-Y. Lu, *Fluid Phase Equil.* **56**:105 (1990).
8. P. Vonka, P. Dittrich, and J. Lovland, *Fluid Phase Equil.* **88**:63 (1993).
9. R. Stryjek and J. H. Vera, *Can. J. Chem. Eng.* **64**:323 (1986).
10. E. Brunner and W. Hultenschmidt, *J. Chem. Thermodyn.* **22**:73 (1990).
11. F. Galivel-Solastiouk, S. Laugier, and D. Richon, *Fluid Phase Equil.* **28**:73 (1986).
12. T. Holderbaum, A. Utzig, and J. Gmehling, *Fluid Phase Equil.* **63**:219 (1991).
13. R. A. Wilsak, W. C. Scott, and G. Thodos, *Fluid Phase Equil.* **33**:157 (1987).
14. W. C. Scott, R. A. Wilsak, and G. Thodos, *J. Chem. Thermodyn.* **19**:449 (1987).
15. H. Huang, S. I. Sandler, and H. Orbey, *Fluid Phase Equil.* **96**:143 (1994).
16. P. T. Eubank, personal communication, Texas A&M University (1993).