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A Field-Space Conformal-Solution Method: Binary Vapor–Liquid Phase Behavior[1]

T. S. Storvick[2,3] and J. R. Fox[2]

The field-space conformal solution method provides an entirely new thermodynamic framework for the description of fluid mixtures in terms of the properties of a pure reference fluid. The utility and performance of the method are examined in the special case of vapor–liquid equilibrium correlation for simple mixtures. This is one of several cases in which field-space methods have numerical or theoretical advantages over methods presently used in mixture property correlation; only properties along the vapor pressure curve of the pure-fluid reference system are required for a complete description of the mixture phase behavior. Vapor–liquid equilibrium data for three binary hydrocarbon mixtures, *n*-butane + *n*-pentane, *n*-butane + *n*-hexane, and *n*-butane + *n*-octane, are correlated with a simple implementation of the method having two independent mixture parameters. Two pure-fluid equations of state, a Peng–Robinson equation and a 32-constant modified Benedict–Webb–Rubin equation, are tested as reference systems. The effects of differences in the quality of the reference system and of a range of mixture component size ratios are examined.

KEY WORDS: conformal solution; hydrocarbon binary mixture; mixture thermodynamics; vapor–liquid equilibrium; vapor–liquid phase behavior.

1. INTRODUCTION

In the preceding paper [1], we introduced a new method, dubbed the "field-space conformal solution method," by which the known thermodynamic properties of a pure-fluid reference system may be used to

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[2] Thermophysics Division, National Institute of Standards and Technology (formerly National Bureau of Standards), Boulder, Colorado 80303, U.S.A.

[3] Permanent address: Chemical Engineering Department, University of Missouri-Columbia, Columbia, Missouri 65211, U.S.A.

correlate, and ultimately to predict, the properties of a mixture target system. The method obeys the constraints of a one-fluid conformal solution theory and may be compared to the van der Waals one-fluid theory and similar corresponding-states constructs. The underlying mathematical structure of the new transformation is fundamentally different, however, and it is through this structural difference that the expected design advantages, both numerical and theoretical, are to be acheived. In this paper tests of the performance of the simplest useful implementation of the transformation method are described, and necessary algorithms for typical engineering calculations are coincidentally developed.

The chosen performance test is the correlation of the high-pressure vapor–liquid equilibrium (VLE) properties of some simple binary mixtures. We of course intend to perform and report far more comprehensive and global testing in the future, but any correlational method that is accurate for VLE may be immediately technically useful, while failure would be fatal for either the particular implementation or the method itself.

The most novel aspect of the field-space conformal solution (FSCS) method is that it maps the VLE states (the dew and bubble surfaces) of a multicomponent mixture onto the vapor pressure curve of the pure-fluid reference system. This is in contrast to the behavior of conventional one-fluid theories which, with the exception of azeotropic critical points, map all VLE states of the mixture onto one-phase states of the reference system. This difference leads to a number of apparent advantages. First, for VLE calculations, the reference system may consist of simple correlations of the appropriate properties along the vapor pressure curve, rather than a complete description of the one-phase region. Second, some calculations are greatly simplified; for example, the location of the critical line can in some implementations of FSCS be solved analytically, while in other one-fluid theories a tedious numerical procedure is required. Third, if a VLE calculation cannot be solved analytically, and requires the use of an iterative numerical procedure, the solution space which must be searched is one-dimensional (the vapor pressure curve) rather than two-dimensional (the one-phase region). Fourth, if the reference system is sufficiently accurate, it will develop that aspect of the behavior of real pure fluids referred to as "critical scaling"; in FSCS that behavior will be transformed into an appropriate mixture critical scaling, while in the traditional methods that behavior would be lost into the interior of the mixture two-phase region.

In this paper, the VLE properties of three *n*-alkane binary mixtures are correlated using the pure-fluid properties of *n*-butane, as described by two common equations of state, as the reference fluid. Accurate VLE data are available for the chosen mixtures over the entire liquid-vapor coexistence region. The reference substance properties were computed using the Peng–Robinson equation, a representative cubic equation of state, and alternatively, the 32-constant modified Benedict–Webb–Rubin equation (MBWR).

2. IMPLEMENTATION

The FSCS transformation equations used to describe the properties of a binary mixture using the properties of a pure-fluid reference system were derived in Ref. 1. To summarize the working equations, the temperature T', pressure p', molar density ρ', and composition x_1' of the mixture can be expressed in terms of the reference-system temperature T, pressure p, molar density ρ, and molar internal energy u (defined below), through the use of a parameter η. The parameter η is related to a ratio of mixture activities and should therefore be recognized as a field variable; that is, η is equal in coexisting phases of the mixture. The four working equations are

$$T' = Tf(\eta) \tag{1}$$

$$p' = pf(\eta)/h(\eta) \tag{2}$$

$$x_1' = \eta - \left[\frac{uf_\eta}{RTf(\eta)} + \frac{ph_\eta}{\rho RTh(\eta)}\right](\eta - \eta^2) \tag{3}$$

$$\rho' = \rho/h(\eta) \tag{4}$$

where $f(\eta)$ and $h(\eta)$ are positive-definite analytic functions of η and where $f_\eta = df/d\eta$, $h_\eta = dh/d\eta$. Note that Eq. (3) is really two equations: one for the mixture's liquid composition calculated from the pure-fluid reference liquid density and internal energy and one for the mixture vapor composition calculated from the reference vapor density and internal energy.

Specifying choices of $f(\eta)$ and $h(\eta)$ and of a temperature-dependent function in the definition of u completes the process we refer to as "implementing" the method. Here we make these choices such that the number of free parameters that must be fitted with mixture data is severely restricted and Eq. (3) is quartic in η and thus may be solved analytically rather than numerically. (In hindsight the latter restriction produces no useful numerical simplification, and should therefore be regarded as arbitrary.) The internal energy in Eq. (3) was computed using the definition

$$u = CRT + \int_0^\rho \left[p - T\left(\frac{dp}{dT}\right)_\rho\right]\frac{d\rho}{\rho^2} \tag{5}$$

The integral is the configurational internal energy and the parameter C is an adjustable parameter. The functions $f(\eta)$ and $h(\eta)$ were taken in this study to be inverse polynomials of the forms

$$f(\eta) = (f_0 + f_1\eta)^{-1} \tag{6}$$

$$h(\eta) = (h_0 + h_1\eta + h_2\eta^2)^{-1} \tag{7}$$

where the f_i and h_i are constants. These functions were chosen on the basis of initial performance, without exhaustive testing, from the set of polynomials, inverse polynomials, and ratios of polynomials that leave Eq. (3) no more than quartic in η. In the correlations reported here, four of the six unknown constants, f_0, f_1, h_0, and the sum $h_0 + h_1 + h_2$, were specified by requiring that the critical line of the mixture reproduce the critical pressures and temperatures of the constituent pure fluids.

With this choice of the functions f and h, the variation of the mixture's critical pressure with temperature along the critical line can be expressed analytically:

$$p'_c(T') = p_{c2}\left\{\frac{h_1}{f_1} + \frac{T'}{T_{c2}}\left[1 - \frac{h_1}{f_1} + \frac{h_2}{f_1^2}\left(\frac{T_{c2}}{T'} - 1\right)^2\right]\right\} \tag{8}$$

where we have adopted the convention that component 1 refers to the constituent fluid with lower critical temperature and where p_{c2} and T_{c2} are the critical pressure and temperature of component 2. The temperature range of the critical line is $T_{c1} < T'_c < T_{c2}$, with T_{c1} the critical temperature of component 1. The critical line is linear in the p', T' space when h_2 is zero.

The saturated liquid and vapor properties of the binary mixture can be calculated given the remaining parameters C and h_2. For example, in a typical bubble- or dew-point calculation, the mixture temperature T' and the liquid composition x' (or vapor composition y') would be given. The corresponding state of the reference system must be on the vapor pressure curve, and therefore all of the reference-fluid properties may be considered a function of one variable, for example, the temperature T. The parameter η and the temperature T can be determined by Eqs. (1) and (3). The mixture mole fractions are confined to the interval $0 \leqslant x'$ (or y') $\leqslant 1$, and there is typically only one real solution η in the interval $0 \leqslant \eta \leqslant 1$ that corresponds to the simultaneous solution of Eqs. (1) and (3). Once η and T have been numerically determined, the state of the reference fluid is known and the remaining mixture saturation properties may be computed directly. The vapor composition y' (or liquid composition x') is calculated by substituting the reference-fluid vapor (or liquid) properties into Eq. (3). Essentially the same technique can be used whenever two of the quantities p', T', x', y', and ρ' are used to specify the state of the mixture.

3. VLE DATA CORRELATION

The three alkane mixtures we chose for the VLE correlation tests are systems for which any useful one-fluid theory should record good results. The mixture *n*-butane + *n*-pentane may be regarded as very closely approaching the ideal conformal solution, while the mixtures *n*-butane + *n*-hexane and *n*-butane + *n*-octane would appear to exercise but a single primitive scale factor, that of molecular volume.

The objective of the fitting process is optimization of the correlation of experimental measurements of mixture properties through variation of the model's free parameters C and h_2. We used experimental VLE data of apparently very high quality from the research group of Webster Kay [3–5]. The data are reported as sets of $p' - T' - \rho'$ points on five or six isopleths ($x' = y' = \text{constant}$) for each mixture. While regression of the data using a suitable measure of the deviation between experimental and calculated points and one of the computational methods described above is straightforward, we used a simpler method based upon the fact that in the FSCS framework the graphical generation of constant-composition dew-bubble curves (that is, liquid–vapor phase boundaries) is mathematically trivial. We prepared a table of the liquid and vapor properties of the saturated reference fluid at small temperature intervals. Given trial values of C and h_2 and one of the experimental compositions, a value of η may be calculated for each table entry from the solution of Eq. (3); from the other working equations p', T', and ρ' are determined directly. The five or six isopleths thus generated, together with the experimental data, may be displayed (for example, by projection into the p, T plane) and the parameters iteratively adjusted to achieve a visual best fit. This process might be further automated and regularized by defining the objective function (that is, the function to be minimized) as the sum of the squared minimum distances between experimental points and generated curves in the p', T' plane or p', T', ρ' space, with the distances calculated by interpolation of the table. We used the simple visual process but optimized the fit in the p, T plane near the critical line. The density data were ignored in the parameter determination.

The properties of saturated pure *n*-butane, used as the reference fluid for the correlations, were computed and tabulated using two well studied pure-fluid equations of state. The Peng–Robinson equation [6] was selected as representative of the cubic equations of state that have been widely adopted in conventional VLE algorithms. The parameters a and b in this equation of state were adjusted so that the critical temperature and critical pressure of the equation matched those of *n*-butane (with the values indicated in the legend to Fig. 1) and the acentric factor appropriate to *n*-butane, $\omega = 0.193$, was taken from Van Ness and Abbott [7].

More accurate reference-system properties were computed using the 32-constant MBWR equation of state, and these were used in separate correlations of the mixture data. The constants for the MBWR equation were those for *n*-butane reported by Younglove and Ely [8]. This equation of state produces saturated densities and configurational energies of much greater accuracy than the Peng–Robinson form, and near the critical point it much more closely mimics the true scaling behavior of the fluid.

4. CORRELATION RESULTS

A correlation of the *n*-butane + *n*-pentane mixture using the Peng–Robinson reference system is shown in Figs. 1 and 2. (In all our figures temperature, pressure, and mass density are reduced with respect to the critical properties of the component with the higher critical temperature.) The fit is similar in quality to that of a conventional one-fluid transformation using the Peng–Robinson equation (with the same choice of parameters) and van der Waals mixing rules. The most serious deviations are in the prediction of liquid densities; the experimental dew–bubble surface in Fig. 2 is extremely flat near the critical line and unlike the parabolic curvature of the reference cubic equation of state.

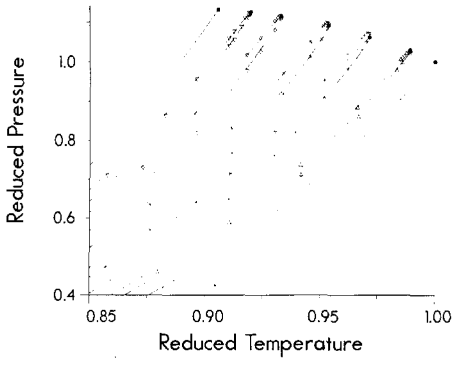

Fig. 1. *N*-Butane + *n*-pentane pure-fluid vapor pressure curves and dew-bubble curves for five mixture compositions shown projected into the p, T plane. Experimental data (symbols) and correlation (lines) calculated using the Peng–Robinson reference system are shown reduced by the critical properties of *n*-pentane. The needed critical point parameters are from Ref. 6: *n*-butane—$T_c = 425.38$ K, $p_c = 3.809$ MPa; *n*-pentane—$T_c = 469.65$ K, $p_c = 3.37$ MPa. The mixture parameters are $h_2 = -0.112$ and $C = 4.5$.

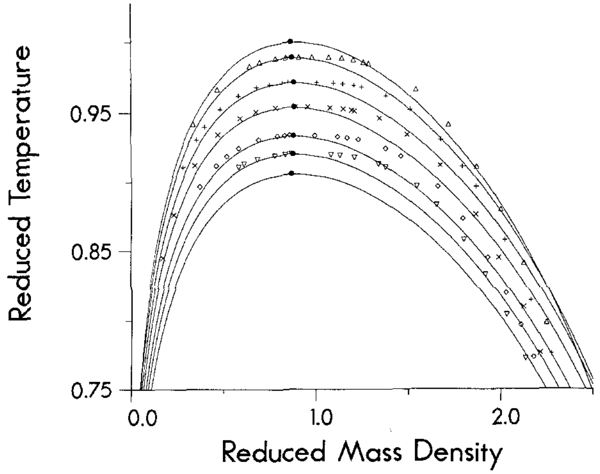

Fig. 2. Calculated (from the correlation indicated in Fig. 1) and experimental *n*-butane + *n*-pentane pure-component and mixture vapor–liquid mass densities reduced by the critical mass density of *n*-pentane.

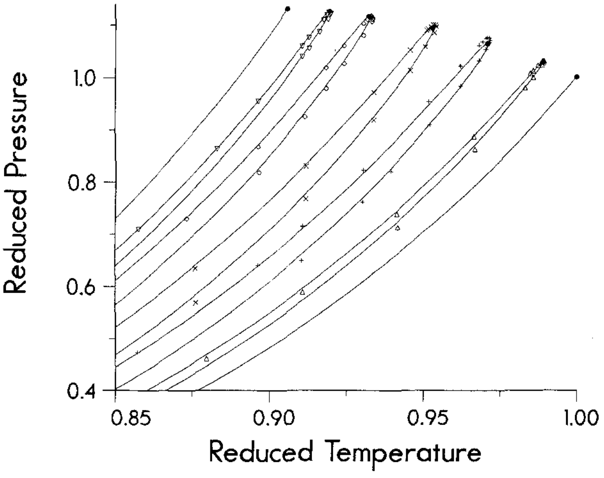

Fig. 3. *N*-Butane + *n*-pentane vapor pressure and dew–bubble curves for five compositions calculated using the MBWR reference system and with all parameter values as in Fig. 1.

The correlation of this same mixture using the MBWR reference equation is shown in Figs. 3 and 4. Figure 3 is but subtly different from Fig. 1; the dew–bubble curves are somewhat wider near the critical line. The contrast between Fig. 2 and Fig. 4 is thus all the more significant; the improvement in the density correlation shown in Fig. 4 is clearly a reflection of the better density correlation of the reference system. (The highest and lowest curves in the figure are the coexistence curves predicted for the pure fluids.) There are still obvious problems; the fit to densities would be nearly perfect if all of the curves were shifted slightly to lower density. The fitting resulted in identical values of C and h_2 for the two reference systems.

In the remaining figures, only the correlations using the MBWR reference system are shown. Figures 5 and 6 show a correlation for *n*-butane + *n*-hexane and Figs. 7 and 8 show a correlation for *n*-butane + *n*-octane. Correlations using the Peng–Robinson reference system are similar except in the predictions of density, where the differences follow the results for *n*-butane + *n*-pentane. These figures reveal three separate problems with our present implementation. The most obvious is the serious overprediction of liquid densities at intermediate compositions shown in Figs. 6 and 8. Second, we do not have sufficient flexibility to fit the critical region of the *n*-butane + *n*-octane mixture or any mixture we have yet studied with larger positive deviations from ideality (as identified by larger convex curvature of the critical line). Third, the fits are uniformly better on the *n*-butane end of the composition spectrum.

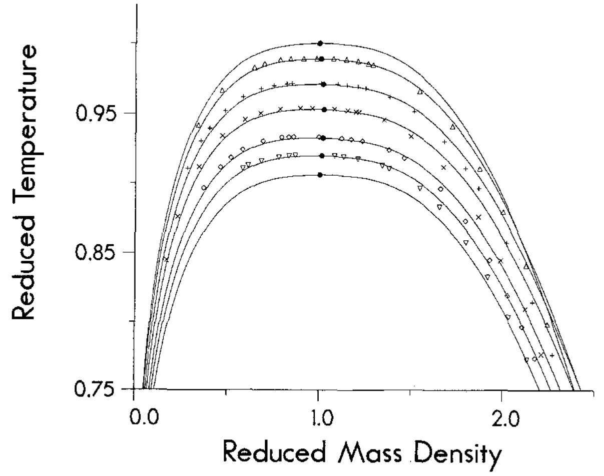

Fig. 4. *N*-Butane + *n*-pentane pure component and mixture vapor–liquid mass densities as calculated with the MBWR reference fluid and the parameter values specified in Fig. 1.

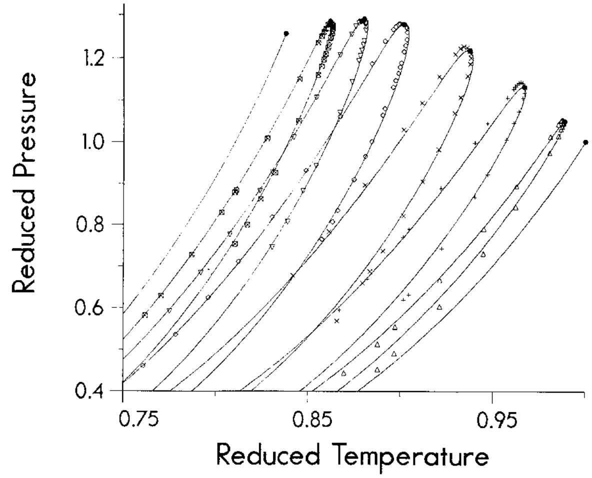

Fig. 5. *N*-Butane + *n*-hexane vapor pressure and dew–bubble curves for six mixture compositions calculated with the MBWR reference system using the additional critical-point parameters for *n*-hexane $p_c = 507.95$ K and $p_c = 3.032$ MPa and mixture parameters $h_2 = -0.55$ and $C = 5.15$.

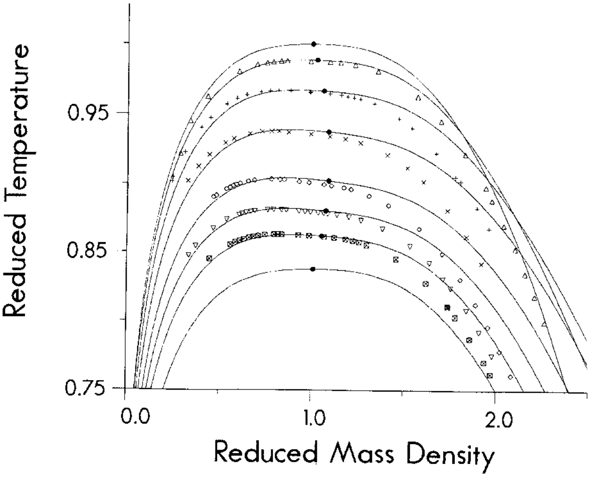

Fig. 6. *N*-Butane + *n*-hexane pure-component and mixture vapor–liquid mass densities as predicted by the correlation shown in Fig. 5.

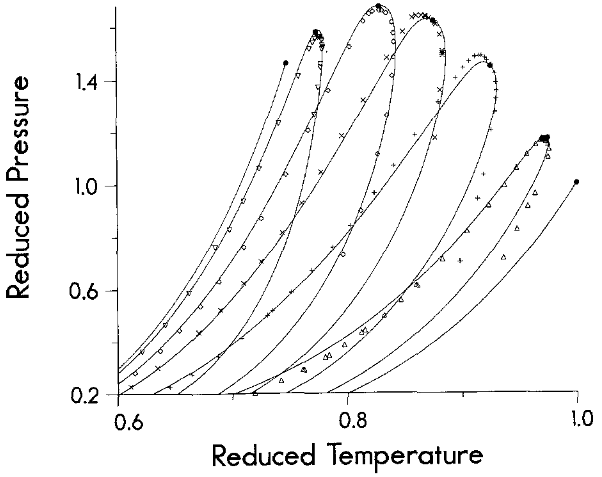

Fig. 7. *N*-Butane + *n*-octane pure-fluid vapor pressure curves and dew–bubble curves for five mixture compositions as calculated with the MBWR reference system using the additional critical-point parameters for *n*-octane $T_c = 569.2$ K and $p_c = 2.603$ MPa and mixture parameters $h_2 = -1.842$ and $C = 5.2$.

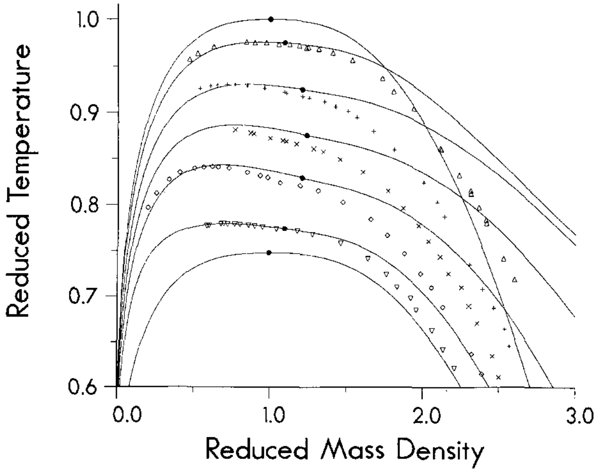

Fig. 8. *N*-Butane + *n*-octane pure-component and mixture vapor–liquid densities as predicted by the correlation in Fig. 7.

5. DISCUSSION AND CONCLUDING REMARKS

The results of this study demonstrate, in prototype, the primary design goals of the FSCS thermodynamic framework. They also reveal some major shortcomings of our present implementation and perhaps of the underlying framework as well. The correlation of *n*-butane + *n*-pentane suggests that a more refined version of FSCS, together with an exacting reference system, may be able to provide very high-quality representations of mixtures of very similar components. On the other hand, we have recorded a very rapid deterioration of correlative ability as the components of the mixture become successively more dissimilar.

Each of the three correlational problems we identified in the previous section appears to stem, at least in part, from the rigidity inherent in the coupling of field-space corresponding-states methodology with a one-fluid conformal solution structure. An example of this inherent rigidity is the fact that, in a one-fluid conformal transformation, the compressibility factor $p/\rho RT$ is identical in target mixture and reference pure-fluid states. In the field-space transformation framework one of the consequences is that all points along the critical line are constrained to a constant compressibility factor equal to that of the reference fluid, while in the conventional method the difference in state-to-state mapping frees the critical line from this constraint. Since we have been fitting the critical line in the p, T plane, the natural variation in the compressibility factor along that line must be compensated by a shifting of critical densities, and this is undoubtedly the major cause of our difficulties with the densities correlations.

A second aspect of one-fluid field-space transformations, which will become much more important when mixtures of quite dissimilar components are considered, is that such transformations cannot produce the liquid–liquid phase separation that is a natural consequence of relatively repulsive interactions between the components. We argue that it is not the role of the transformation machinery to introduce the effect of forces not represented in the reference system. But we are led by that reasoning to the conclusion that the reference systems for such mixtures must themselves be mixtures with the requisite types of molecular interactions. The generalization of our present work to use mixture reference systems is straightforward, but the utility of such a generalization appears to be limited by lack of suitable reference systems and the probable loss of the numerical advantages the one-fluid implementation enjoys.

We hope to greatly improve the one-fluid form by breaking the structure of conformality with the addition of "background" transformation terms of the type introduced in an earlier version of the theory [9] and by other devices designed to enhance our ability to describe positive deviations from ideality at minimum cost in additional parameters. Whatever the outcome of that plan, the eventual transition to methods based upon mixture reference systems is, we think, an inevitable step in any successful future development of field-space transformation methods.

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