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Critical Lines for Type-III Aqueous Mixtures by Generalized Corresponding-States Models[1]

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An algorithm has been developed for calculating the gas–gas critical line of type-III binary fluid mixtures for extended corresponding-states (ECS) models. The algorithm searches for an extremum in pressure on the spinodal curve of an isothermal pressure–composition phase diagram of a binary mixture. The method has been applied to solutions of carbon dioxide and of nitrogen in water, starting at the water critical point. Two variants of ECS have been tested for their ability to represent reliable $PVTx$ data in the nitrogen–water mixture. It is demonstrated that in the latter system both ECS variants produce an artifact in the gas–gas critical line in the range of 0–0.2 mole fraction of nitrogen.

KEY WORDS: aqueous mixtures; carbon dioxide; critical lines; extended corresponding states; gas–gas equilibrium; nitrogen; type III mixtures.

1. INTRODUCTION

The two-parameter equation of state of van der Waals, generalized to binary mixtures by means of the principle of corresponding states, although not an accurate predictor of fluid properties, has been able to produce all

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but one of the types of phase behavior known to exist. In particular, it has been able to yield the type-III phase diagrams, in the classification of Van Konynenburg and Scott [1], for which type the critical line extending from the critical point of the more volatile component is interrupted by a nearby three-phase line (liquid–liquid–vapor), while the branch of the critical line emanating from the critical point of the less volatile component, usually denoted as a gas–gas critical line, ultimately passes to high pressures. It may immediately move to higher pressures, with or without passing through a minimum in temperature. It may also move to lower temperatures first, while exhibiting a maximum followed by a minimum in pressure (type IIIm).

Components with a substantial difference in their critical temperatures and pressures tend to have interrupted critical lines. Type-III behavior, with a temperature minimum in the gas–gas critical line, is prevalent if constituents such as nitrogen, argon, oxygen, methane, or carbon dioxide, with critical temperatures ranging from cryogenic to ambient temperature, are mixed with water, which has a critical temperature near 647 K. New technologies such as hydrothermal oxidation, that use supercritical water as a reaction medium, have spurred interest in thermodynamic modeling of these systems.

The principle of corresponding states uses two constant scale factors, for volume and temperature, respectively, to map the properties of one component onto those of the second; these scale factors are related to the ratios of the energy and length parameters characterizing the molecular interactions of the two components. Mixture properties are similarly mapped, but the scale factors are functions of composition, usually involving at least two more adjustable "interaction" parameters, $l_{i,j}$, related to the volume scale factor, and $k_{i,j}$, related to the temperature scale factor. In the applications following, a one-fluid approach is used, which means that the mixture properties are mapped onto those of one pure reference fluid.

Given the complexity of the water solvent, there is no hope for straightforward application of two-parameter corresponding states. Generalizations, however, known as "extended corresponding states (ECS)" [2, 3] have been used successfully in the past for modeling mixtures of some complexity. The departures from corresponding states are incorporated by means of two "shape factors," smooth, slowly varying functions of the thermodynamic state variables. The NIST SUPERTRAPP program [2] uses a few-parameter empirical temperature dependence of the shape factors, with one reference fluid, propane. Phase coexistence and critical lines have been determined for SUPERTRAPP with density-independent shape factors [4]. The NIST14 Database [3] uses high-quality thermodynamic surfaces for each constituent, and calculates the shape factors point by point such as to guarantee an "exact" mapping for the pure components. This model is applied in the one-fluid mode.

ECS methods have been recently employed for modeling some near- and supercritical aqueous systems. Thus, Fenghour et al. [5] fitted their $PVTx$ data and dew points for nitrogen in water by means of an ECS "exact shape factor" one-fluid model, with accurate equations of state for both components in the binary, while Gallagher et al. modeled the systems carbon dioxide in water [6] and nitrogen in water [7] by a one-fluid model, with the NBS/NRC Helmholtz free energy of water as the reference [8], with approximate shape factors that are simple functions of density and temperature and with a total of eight adjustable parameters. Gallagher et al. did not use a detailed thermodynamic formulation for the second component. They did calculate critical lines and phase boundaries for their ECS model; they reported an artifact for the critical line of the nitrogen–water system that is not observed experimentally [7].

The present paper specifically addresses the question of the shape of the type-III critical line for two ECS models with density-dependent shape factors: the "approximate shape factor" variant of Gallagher et al. [6, 7] and the "exact shape factor" variant of NIST14 [3] and of Fenghour et al. [5]. It cannot be taken for granted that the simple critical lines generated for binary mixtures by the van der Waals equation and consistent with experimental evidence will also be a feature of more complex equations of state. In fact, warnings about new types of phase behavior have been sounded in the literature recently with respect to equations of state more complex than cubic equations [9]. The Helmholtz free energies used in ECS models are much more complex, with as many as 30–60 parameters, so that new features in the phase behavior are not unlikely.

For a mathematical description of the "approximate" and the "exact shape factor" ECS models, we refer to the literature [6, 10]. In Section 2, both types of ECS models are tested as to their ability to fit $PVTx$ data in the homogeneous region of aqueous systems. As an example, we use the available three sets of $PVTx$ data for the system nitrogen–water [5, 11, 12], which have been demonstrated to be mutually consistent [7], and have also been studied by Fenghour et al. [5]. In Section 3, we study the gas–gas critical line generated by each model for the two systems: carbon dioxide in water and nitrogen in water. We discover an artifact, in the latter system, that is common to both models. In Section 4, we summarize our conclusions regarding the usefulness of ECS for modeling near- and supercritical aqueous systems.

2. *PVTx*, THE HOMOGENEOUS REGION OF NITROGEN–WATER

Gallagher et al. [7] fitted the eight parameters in their approximate shape-factor model to the three sets of *PVTx* data available for nitrogen in water: those of Fenghour et al., from 428 to 698 K for pressures below 31 MPa [5]; those of Abdulagatov et al., from 523 to 663 K, up to 70 MPa [11]; and those of Japas and Franck, at 673 K and up to 290 MPa [13]. In all cases, the entire composition range was spanned. Figure 1 shows the comparison of the data with the optimized model and demonstrates that the three data sets are basically consistent. The model fits 90% of the composite data with a spread of ±3% in density, but does not fit the data of Fenghour et al. [5] to within their claimed uncertainty of 0.1%. Figure 2 shows the results of a comparison of the same data sets with the "exact shape factor" model, where the interaction parameter $k_{i,j}$ was set equal to 1.17 and $l_{i,j}$ equal to 0.84. For the data of Fenghour et al., we note the same systematic trends, and a somewhat larger spread, from −1% to +6% in density. The data at the higher pressures deviate systematically. Fenghour et al. [5] made a similar comparison, in the range up to 55 MPa, for the equivalent ECS model. The deviation pattern of their own data from their model is similar to ours, but the data at higher pressure depart in the opposite direction. This comparison, however, is quite sensitive to the choice of the volume-related interaction parameter, $l_{i,j}$, and choosing $l_{i,j}$ close to unity would reduce the systematics at the higher

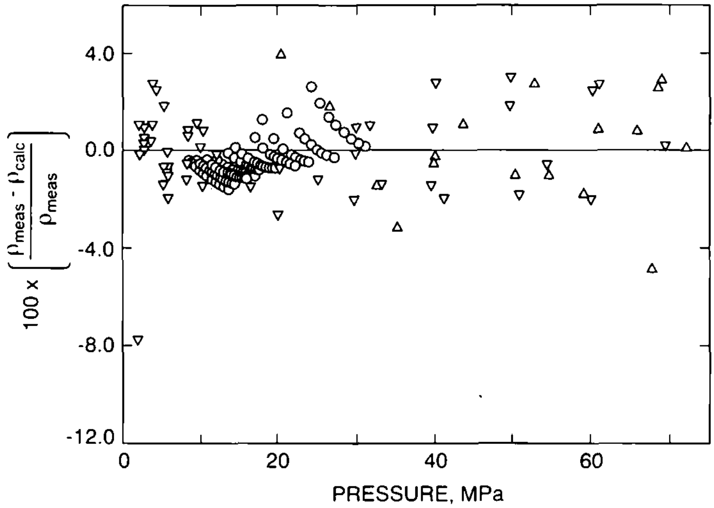

Fig. 1. For nitrogen–water, percentage deviations of the experimental densities from the ECS model of Gallagher et al. [6]. Data: ○, Ref. 5; ▽, Ref. 11; △, Ref. 13.

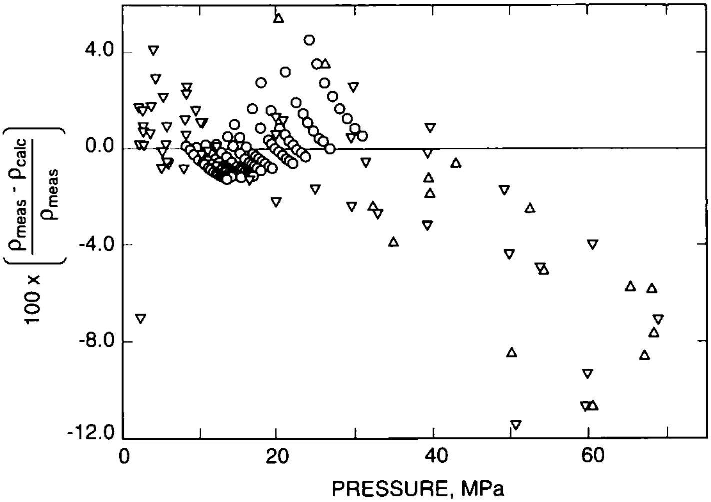

Fig. 2. For nitrogen water, percentage deviations of the experimental densities from the "exact-shape-factor" ECS model, with $k_{i,j} = 1.17$, $l_{i,j} = 0.84$. Data: . Ref. 5; ▽, Ref. 11, △, Ref. 13.

pressures. There is, however, a good reason not to choose l_{ij} close to unity, as discussed in Section 3.

The "exact shape factor" model, with two adjustable parameters, has far less flexibility than the "approximate shape factor" model, with eight. On the other hand, the "exact shape factor" model has the full equation of state of nitrogen built in, as well as that of water, whereas the approximate "shape factor model," based solely on the equation of state of water, is not accurate at the pure-nitrogen end.

We conclude that, even with high-quality starting equations of state for the pure components, with experimental uncertainties no larger than a few parts in 1000 in the density, considerable uncertainty is introduced when the ECS model is generalized to aqueous mixtures. The quality of the data of Ref. 5 is not done justice, the departures being systematic and at least an order of magnitude larger than the claimed uncertainty. This conclusion should be counterbalanced by the consideration that most engineering equations of state fail in a major way in representing the density of high-pressure mixtures in the supercritical regime. A model that can yield mixture densities with a reliability of a few percent will still be very useful for many applications, such as hydrothermal oxidation, where engineers currently have no way of estimating the density from pressure, temperature, and composition data of multicomponent supercritical aqueous mixtures.

3. THE CRITICAL LINES FOR NITROGEN OR CARBON DIOXIDE IN WATER

The mixture critical point is obtained from the Gibbs conditions

$$\left(\frac{\partial^2 G}{\partial x^2}\right)_{p,T} = 0 \qquad \left(\frac{\partial^3 G}{\partial x^3}\right)_{p,T} = 0 \tag{1}$$

where G is the Gibbs free energy, x the mole fraction, p the pressure, and T the temperature. The second derivative of the Gibbs free energy can be related to the matrix of second derivatives of the Helmholtz free energy as determined numerically from the ECS models described above. For the present application, we have used the following automated procedure to locate a point on the critical line at a chosen temperature. For a selected input composition, the algorithm searches for the density and pressure of the state point at which the first Gibbs condition is satisfied. The process

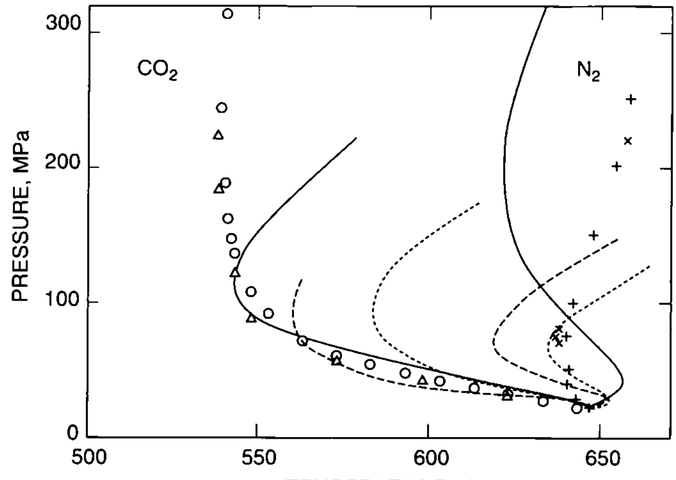

Fig. 3. The representation of the critical curves of carbon dioxide in water (CO_2) and of nitrogen in water (N_2) in p–T coordinates, by the two ECS models. ——, Approximate shape factors. For the "exact-shape-factor" model, several choices of mixing parameters were used, as indicated. CO_2 solute data: △, Ref. 14; ○, Ref. 12; ···, $k_{i,j} = 1.02$ and $l_{i,j} = 0.90$; ---, $k_{i,j} = 1.09$ and $l_{i,j} = 0.85$. N_2 solute data: +, Ref. 13; ×, Ref. 16; ···, $k_{i,j} = 1.17$ and $l_{i,j} = 0.84$ (as in Fig. 2); ---, $k_{i,j} = 1.15$ and $l_{i,j} = 0.75$. In all model cases, the initial behavior of the nitrogen–water critical line contradicts experimental evidence.

is repeated for an increment in composition. The locus of such points is the isothermal "spinodal curve." The pressure of the spinodal points reaches an extremum as a function of composition at criticality. Although the isothermal dew-bubble envelope and spinodal are convex upward in many applications, in gas–gas equilibrium with a temperature minimum, they begin convex upward at the critical point of the nonvolatile component, but they turn convex downward after the minimum is passed.

The gas–gas critical line so obtained by each of the two ECS models for carbon dioxide in water is shown in Fig. 3 in p–T coordinates. The data are those of Takenouchi and Kennedy [14] and of Tödheide and Franck [12], the latter recently confirmed by new measurements by Mather and Franck [15]. The model of Gallagher et al. [6] does a good job on the initial part of the critical curve before it passes through a temperature minimum. The "exact shape factor model" has been used with several choices of mixing parameters, see Fig. 3. None of these do well on the initial part of the critical line, but the behavior at extreme pressures is much more acceptable than that of the model of Gallagher et al. [6].

The gas–gas critical line for the system nitrogen–water is also shown in Fig. 3. The data are from Japas and Franck [13] and from Tsiklis et al. [16]. In this case, Gallagher et al. [7] had noted an unobserved initial rise in the critical temperature, preceding the minimum that has been experimentally established. This same feature appears to be present in the "exact-shape-factor" ECS model, for the parameter choices indicated in the caption of Fig. 3. This feature precludes an accurate fit of the critical line and leads to unwanted regions of closed-loop phase coexistence at temperatures within 10 K of the water critical point. Choosing $l_{i,j}$ near unity, as preferred by the $pVTx$ data, gives a critical line much further from the data.

4. CONCLUSIONS

Two types of ECS equations applied to two binary aqueous mixtures in a large region around the water critical point have been shown to predict mixture densities to within a few percent uncertainty but not to within experimental uncertainty. For the carbon dioxide–water system, neither variant does an outstanding job on the critical line, one fitting the low concentrations better, the other the higher concentrations. Similar to the experience of Eaton et al. with a variant of SUPERTRAPP [17] and for nonaqueous systems, we cannot find a set of interaction parameters in the exact-shape-factor model such that it simultaneously represent the $pVTx$ data and the critical curve for the nitrogen–water system (in which the difference in critical temperatures is extremely large). In the critical curve, an unphysical maximum, followed by a minimum, appears in the critical temperature in the composition range of 0–20 mol% nitrogen for both variants of the ECS model. We are investigating whether this artifact is due to the equation of state of water we used, whether it is a peculiarity associated with the unusual properties of water, or whether it is a general feature of ECS when component critical temperatures are very different.

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