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Critical Transitions of Ternary Mixtures: A Window on the Phase Behavior of Multicomponent Fluids[1]

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The critical properties of the carbon dioxide + ethylene + helium ternary mixture are calculated and compared with experimental data. The purpose of the analysis is to illustrate how the calculation of ternary critical transitions can provide an insight into the general fluid phase behavior of multicomponent mixtures. Previous calculations had indicated that ternary mixtures exhibit some critical transitions which have no direct parallel in binary-mixture phase equilibria. Apart from the possibility of a tricritical point, the occurrence of a critical transition between different two-phase regions is likely to be common in ternary mixtures containing, at least, two binary subsystems of limited miscibility. The calculations are in qualitative agreement with available experimental data and they confirm the existence of a "double critical point."

KEY WORDS: carbon dioxide; critical transitions; equations of state; ethylene; helium; ternary mixtures.

1. INTRODUCTION

The fluid phase behavior of many two-component mixtures has been comprehensively studied [1-3] over a wide range of both pressure and temperature. In contrast, the experimental study of three- or more-component mixtures is typically limited to isothermal and isobaric measurements either at or near atmospheric conditions. This absence of data can be partly

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attributed to the great increase in resources that are required to investigate comprehensively multicomponent phase equilibria. Consequently, the basis of our knowledge of multicomponent mixtures is confined largely to observations of two-component phase equilibria typically involving only two phases. It is in this context that the calculation of critical properties has a valuable role in elucidating multicomponent phase equilibria. A critical transition occurs when all of the physical properties of coexisting phases become identical. The nature of the critical transition is a good indicator of the global nature of the phase behavior of the fluid, as exemplified for binary fluid mixtures by the work of van Konynenburg and Scott [4]. van Konynenburg and Scott classified the phase behavior of binary mixtures into five or six broad types based on the topology of critical lines. From the nature of the different critical transitions, the existence of vapor–liquid, liquid–liquid, and liquid–liquid–vapor equilibria can be inferred. Furthermore, the coordinates of a critical point define the absolute limit of multiphase fluid–fluid coexistence.

The phase behavior of binary mixtures provides a useful but limited insight into the nature of the phase behavior of multicomponent fluid mixtures in general. It is probable that phenomena exhibited by ternary mixtures are more representative of multicomponent fluid phase equilibria than binary fluid behavior. Although the complete experimental characterization of a ternary mixture is a daunting undertaking, comprehensive calculations of the ternary critical surface are feasible. These calculations can be of value in elucidating the different types of phase equilibria exhibited by ternary mixtures, thereby providing a window on the phase behavior of multicomponent fluids.

A considerable diversity of critical equilibria can be potentially observed in ternary mixtures. Sadus [5, 6] has reported the following types of critical transitions based on a phenomenological interpretation of critical calculations.

(a) Class 1: Multiphase critical points (i.e., tricritical, tetracritical, etc.) involving three or more phases undergoing a simultaneous transition to produce a single homogeneous phase. In the case of a tricritical point, the two menisci signifying the phase boundaries disappear simultaneously.

(b) Class 2: Lower-critical solution phenomena (LCST) and gas–liquid critical transition meet at a relatively low temperature. A critical transition occurs transforming the two-phase liquid–liquid equilibrium into a two-phase gas–liquid equilibrium. That is, the meniscus between the two liquid phases becomes critical simultaneously with the formation of a gas–liquid meniscus.

(c) Class 3a: A region of lower critical solution temperature (LCST) and upper critical solution temperature (UCST) meet. The resulting critical transition is between the two-phase liquid–liquid equilibria. That is, the lower solution meniscus disappears with the simultaneous formation of an upper critical solution meniscus.

(d) Class 3b: There is a transition between two different two-phase upper critical solution menisci.

Experimental data for the critical transitions of ternary mixtures are extremely rare and typically confined to the vapor–liquid critical transition. A compilation of the gas–liquid critical transitions of approximately 60 ternary mixtures measured between the years 1945 and 1991 is available [7]. The data of Tsiklis et al. [8] for the carbon dioxide + ethylene + helium mixture are of particularly interest. They reported critical transitions of this ternary system over a significant range of composition, temperature, and pressure. The objective of the work reported here is to determine the critical surface for carbon dioxide + ethylene + helium and to compare the calculations with the available experimental data in order to verify both the accuracy of theory and, where possible, the existence of some of the above-postulated critical transitions.

2. THEORY

The theoretical methodology has been described elsewhere [7, 9], and therefore only a general outline is presented below. The critical transition of an m-component fluid can be obtained by determining the temperature (T), volume (V), and composition (x) which satisfy the following criteria [10]:

$$W = \begin{vmatrix} -(\partial^2 A/\partial V^2)_T & -(\partial^2 A/\partial x_1\,\partial V)_T & \cdots & -(\partial^2 A/\partial x_{m-1}\,\partial V)_T \\ (\partial^2 A/\partial x_1\,\partial V)_T & (\partial^2 A/\partial x_1^2)_{T,V} & \cdots & (\partial^2 A/\partial x_1\,\partial x_{m-1})_{T,V} \\ \cdot & \cdot & & \cdot \\ \cdot & \cdot & & \cdot \\ (\partial^2 A/\partial x_{m-1}\,\partial V)_T & (\partial^2 A/\partial x_{m-1}\,\partial x_1)_{T,V} & \cdots & (\partial^2 A/\partial x_2^2)_{T,V} \end{vmatrix} = 0 \qquad (1)$$

$$X = \begin{vmatrix} (\partial W/\partial V)_T & (\partial W/\partial x_1)_{T,V} & \cdots & (\partial W/\partial x_2)_{T,V} \\ (\partial^2 A/\partial x_1\,\partial V)_T & (\partial^2 A/\partial x_1^2)_{T,V} & \cdots & (\partial^2 A/\partial x_1\,\partial x_2)_{T,V} \\ \cdot & \cdot & & \cdot \\ \cdot & \cdot & & \cdot \\ (\partial^2 A/\partial x_2\,\partial V)_T & (\partial^2 A/\partial x_1\,\partial x_2)_{T,V} & \cdots & (\partial^2 A/\partial x_2^2)_{T,V} \end{vmatrix} = 0 \qquad (2)$$

$$Y = \begin{vmatrix} (\partial X/\partial V)_T & (\partial X/\partial x_1)_{T,V} & \cdots & (\partial X/\partial x_2)_{T,V} \\ (\partial^2 A/\partial x_1 \partial V)_T & (\partial^2 A/\partial x_1^2)_{T,V} & \cdots & (\partial^2 A/\partial x_1 \partial x_2)_{T,V} \\ \cdot & \cdot & & \cdot \\ \cdot & \cdot & & \cdot \\ (\partial^2 A/\partial x_2 \partial V)_T & (\partial^2 A/\partial x_1 \partial x_2)_{T,V} & \cdots & (\partial^2 A/\partial x_2^2)_{T,V} \end{vmatrix} > 0 \tag{3}$$

where A denotes the Helmholtz function. In our case, A was obtained from conformal solution theory [11, 12] by means of either the Guggenheim or the Heilig–Franck equation of state. The equation of state proposed by Guggenheim [13] is an example of an accurate hard-sphere model which has been used previously for the calculation of critical equilibria.

$$p = RT/V(1 - b/4V)^4 - a/V^2 \tag{4}$$

Equation (4) has been used to predict the critical properties of a diverse range of binary mixtures [7, 9]. Despite the diversity of the systems studied, good results were consistently reported for the gas–liquid critical locus. The critical liquid liquid equilibria of Type II mixtures was also adequately represented. In contrast, calculations involving Type III equilibria are typically only semiquantitative [14] because of the added difficulty of predicting the transition between gas–liquid and liquid–liquid behavior. The Guggenheim equation has also recently proved valuable in calculating both the gas liquid critical properties [15] and general critical transitions of ternary mixtures [7].

The Heilig–Franck [16] equation employs a temperature-dependent Carnahan–Starling hard-sphere repulsive term [17] plus a Padé approximation of the attractive contribution of virial coefficients of a square-well fluid,

$$p = RT(1 + \beta/V + \beta^2/V^2 - \beta^3/V^3)/V(1 - \beta/V)^3 + RTB/V^2(1 + C/BV) \tag{5}$$

where B and C are the second and third virial coefficients of a square-well fluid, respectively. Accurate calculations of the critical properties of both binary and ternary mixtures [18] have been reported.

The equation-of-state parameters for mixture properties were obtained from the one-component critical data (i.e., $a_{11} = 1.357RT^c_{11}V^c_{11}$ and $b_{11} = V^c_{11}/1.9748$) by applying the one-fluid mixture prescriptions of the type:

$$a = \sum_i \sum_j x_i x_j a_{ij} \tag{6}$$

$$b = \sum_i \sum_j x_i x_j b_{ij} \tag{7}$$

They are based on the implicit assumption that the radial distribution functions of the components are identical and they both explicitly contain a contribution from interactions between dissimilar molecules. The results obtained from the van der Waals mixing rules compare well with computer simulation data if the size difference between the component molecules is not too great [19].

The unlike contributions to the equation-of-state parameters were obtained by applying suitable combining rules.

$$a_{ij} = \xi_{ij} b_{ij} (a_{ii} a_{jj} / b_{ii} b_{jj})^{0.5} \tag{8}$$

$$b_{ij} = 0.125 \zeta_{ij} (b_{ii}^{1/3} + b_{jj}^{1/3})^3 \tag{9}$$

The ξ_{ij} and ζ_{ij} terms are frequently introduced into combining rules in order to optimize the agreement between theory and experiment. The influence of combining rules on phase equilibria calculations has been examined elsewhere [20]. The ξ_{ij} parameter is commonly interpreted as reflecting the strength of the unlike intermolecular interaction. This interpretation is supported by the fact that values of ξ_{ij} obtained from the analysis of the critical properties of many binary mixtures consistently decline with increasing size difference between the component molecules as detailed elsewhere [7, 9].

3. RESULTS AND DISCUSSION

A feature of our calculation of ternary-mixture critical properties is that the required experimental inputs are limited to the critical properties of the individual component fluids and the binary interaction parameters (ξ_{ij} and ζ_{ij}) obtained from the analysis of the three binary subsystems. In this case, we must first consider the phase behavior of the binary carbon dioxide + ethylene, helium + carbon dioxide, and helium + ethylene subsystems.

The phase behavior of carbon dioxide + ethylene is relatively straightforward. Rowlinson et al. [21] reported a continuous critical curve linking the critical points of carbon dioxide and ethylene corresponding to Type I behavior in the van Konynenburg and Scott classification scheme. In contrast, binary mixtures containing helium [22] typically exhibit so-called "gas–gas" immiscibility of the first kind [1, 23, 24]. The critical locus commencing from the critical point of the component with the highest critical temperature extends directly to still higher temperatures and pressures without first passing through a temperature minimum. The phenomenon of "gas–gas" immiscibility of the first kind has been reported for both the helium + ethylene [25] and the helium + carbon dioxide [26] systems to the extraordinary pressure of 800 MPa.

The comparison of theory with experiment for the three binary subsystems is illustrated in Fig. 1 and the resulting interaction parameters are summarized in Table I. The best-fit values of ξ and ζ were obtained by repeatedly calculating the critical locus with different values of the adjustable parameters until optimal agreement was obtained with the experimental p–T data. Good agreement was also obtained for the p–x and T–x behavior of the carbon dioxide + ethylene mixture. It is probable, judging by previous work [9], that the p–x and T–x behavior of the remaining binary subsystems is also predicted with a reasonable degree of accuracy. However, there are insufficient experimental data to confirm this

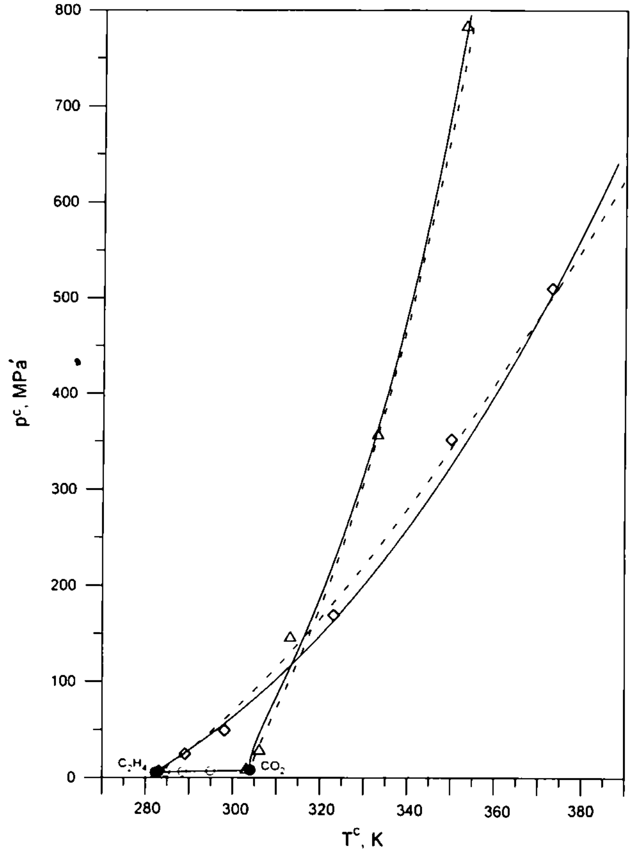

Fig. 1. Comparison of calculations using the Heilig–Franck (-----) and Guggenheim (——) equations of state with experimental data for the binary carbon dioxide + ethylene (○ [21]), helium + ethylene (◇ [25]), and helium + carbon dioxide (△ [26]) mixtures. The critical points (●) of carbon dioxide and ethylene are also illustrated.

Table I. Interaction Parameters Obtained from the Analysis of Binary Mixtures Using the Heilig–Franck and Guggenheim Equations of State

	ξ_{12}		ζ_{12}	
Binary mixture	Heilig–Franck	Guggenheim	Heilig–Franck	Guggenheim
Helium + carbon dioxide	1.850	1.685	1.015	1.012
Helium + ethylene	1.570	1.250	1.064	1.050
Carbon dioxide + ethylene	0.960	0.962	0.940	1.000

and it is likely that the predictions at very high pressure are less reliable than results obtained at low to moderate pressures. The Guggenheim and Heilig–Franck equations of state are of equal accuracy for the critical locus of the carbon dioxide + ethylene mixture. Similarly, calculations by means of these equations of state for both the helium + carbon dioxide and the helium + ethylene systems are also in good agreement with experimental data. In view of the similar accuracy of both equations of state for the binary mixture properties, the simpler Guggenheim equation was adopted in preference to the Heilig–Franck equation for all subsequent ternary mixture calculations.

Tsiklis et al. [8] have reported experimental phase behavior measurements and some critical transition data for the carbon dioxide + ethylene + helium ternary mixture. They reported a partial critical surface for the mixture and isothermal critical properties at 286.15, 293.15, 313.15, 333.15, and 343.15 K. The phase behavior at 286.15 K is of particular interest. Below 20 MPa, only a single two-phase region stemming from the helium + carbon dioxide binary mixture is apparent. So-called "gas–gas" immiscibility in the helium + ethylene system commences at 20 MPa, and thereafter two distinct heterogeneous regions are observed emanating from the helium + carbon dioxide and helium + ethylene binary subsystems. At 30 MPa these two heterogeneous regions have a common critical point, and a single, large two-phase region is created.

To obtain the critical surface of the carbon dioxide + ethylene + helium ternary mixture, several different *slices* were calculated corresponding to different fixed carbon dioxide/ethylene composition ratios. These varying cross-sectional profiles form the basis of the critical surface illustrated in Fig. 2. The ternary critical surface is bounded on three sides by the critical loci of the binary subsystems. The region of "gas–gas" immiscibility evident in the helium + carbon dioxide and helium + ethylene binary mixtures is not as extensive in the ternary system. The addition of a third component increases the miscibility of the system. The shape of the

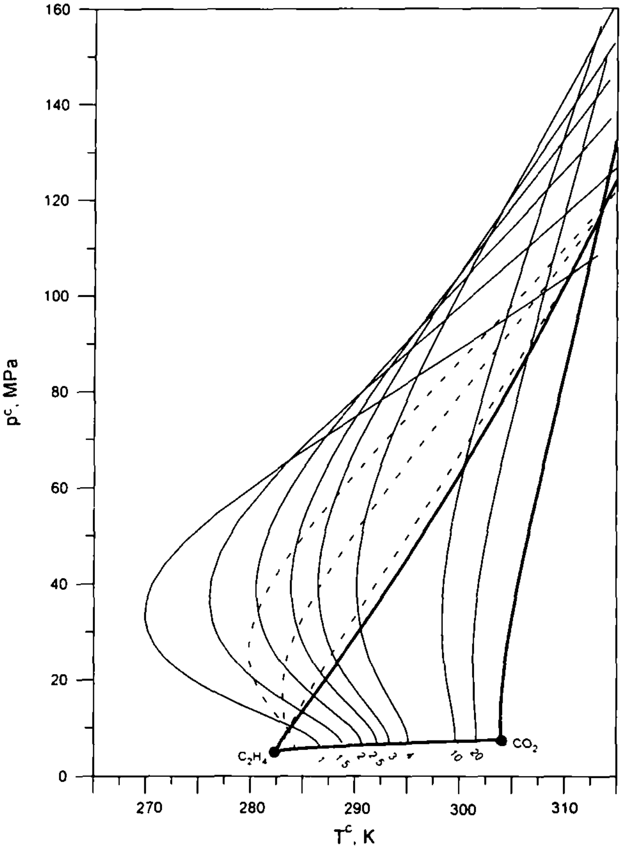

Fig. 2. The calculated critical surface of the carbon dioxide + ethylene + helium ternary mixture. The labels indicate the contribution from the various cross-sectional profiles at a constant carbon dioxide/ethylene ratio. Calculations for ratios < 1 are illustrated by the unlabeled broken lines. The critical properties of the binary subsystems (——) and the critical points (●) of ethylene and carbon dioxide are also illustrated.

ternary surface is akin to a billowing sail. Commencing from the carbon dioxide + ethylene critical locus, the ternary critical surface extends to initially lower temperatures, before passing through a temperature–pressure minimum and proceeding to higher temperatures and very high pressures. The calculated critical surface is consistent with the experimental data reported by Tsiklis et al. [8].

A comparison of theory with the experimental data of Tsiklis et al. for the critical isothermal-composition behavior of the ternary mixture is

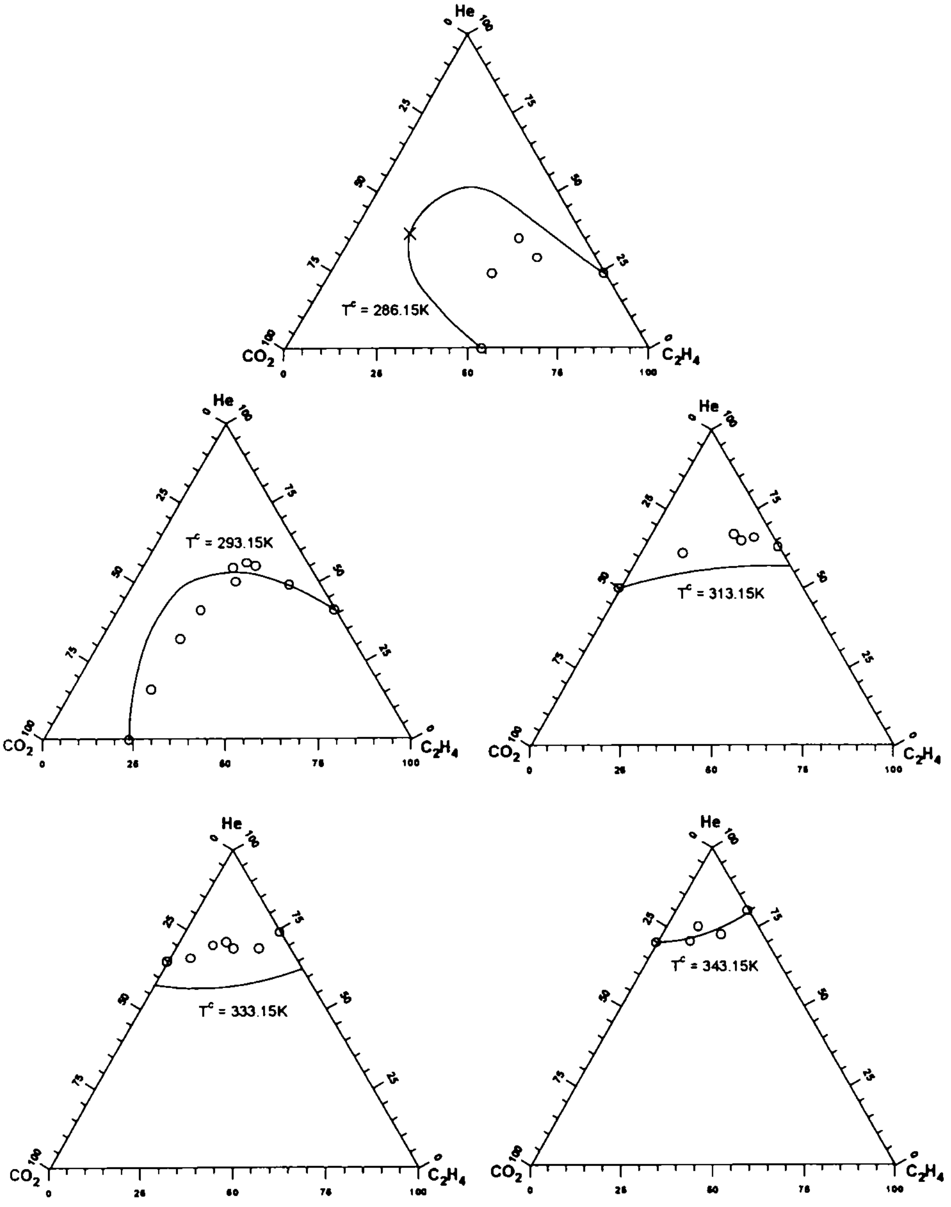

Fig. 3. Comparison of calculations (——) with the experimental data of Tsiklis et al. (○ [8]) for the isothermal-composition behavior of the ternary mixture carbon dioxide + ethylene + helium at various temperatures. The position of a double critical point at 286.15 K is indicated (×).

illustrated in Fig. 3. The ternary calculations are genuine a priori predictions without any reliance on experimental ternary data. It should be noted that Tsiklis et al. directly measured the critical temperature and pressure but they estimated only the critical composition. A "double critical point" was reported at 286.15 K. The calculations confirm the existence of such a transition at this temperature but there is a disparity in the corresponding critical pressure and composition (the predicted coordinates are: $x_{C_2H_4} = 0.158$, $x_{CO_2} = 0.474$, $x_{He} = 0.368$, $V^c = 54.10\ \mathrm{cm^3 \cdot mol^{-1}}$, $p^c = 40.54\ \mathrm{MPa}$). It is apparent from Fig. 3 that theory and experiment at 286.15 K are in only qualitative agreement. The predicted one-phase region is substantially greater than that observed experimentally. The calculations are also in qualitative agreement with experiment at 293.15, 313.15, 333.15, and 343.15 K but the discrepancy between theory and experiment is less serious. At 313.15 and 333.15 K, the accuracy of the ternary analysis is hampered by the inaccuracy of the calculated critical composition for the binary mixtures.

4. CONCLUSIONS

The calculated critical properties of the carbon dioxide + ethylene + helium mixture are in qualitative agreement with the available experimental data. The comparison of theory with experiment also validates the existence of a "double critical point." Calculations of the critical surface of the ternary mixture illustrates the utility of theory both to supplement experimental data and to extend our knowledge of multicomponent equilibria.

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