Thermodynamic Analysis of the Phenomenon of Double Retrograde Vaporization

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The phenomenon of double retrograde vaporization (DRV) is explained on the basis of infinite-dilution critical phenomena. It is shown that the peculiar double-domed or inverse "S" shaped dew point curve distinctive of DRV arises from the conflicting requirements at infinite-dilute versus critical conditions. The argument is general and takes into account both classical and nonclassical behavior. The transitions from subcritical temperatures through double retrograde behavior to normal retrograde condensation at higher temperatures are also explained on the basis of infinite-dilution critical anomalies. The criterion for the existence of DRV is given based on the volumetric properties of the two phases in equilibrium.

Introduction

The development of supercritical fluid applications has been rapidly increasing in the past decade. Many of these applications involve dilute solutes dissolved in supercritical solvents, for example, in supercritical extraction. An important requirement in such developments is knowledge of the thermodynamic properties of these systems. In the near-critical region, the correct understanding of such properties is of particular significance as they can assume highly nonlinear behavior for very dilute mixtures, for example, a strong divergence in the partial molar volume of the solute, a curious concentration dependence of the excess enthalpy, large negative values of apparent molar heat capacities, steep increases in supercritical solubility with changes in temperature or pressure, and path dependence of thermodynamic derivatives such as the partial molar volume.[1] Such distinctive features have been the subject of numerous studies in recent literature. Levelt Sengers[2] and Chimowitz and Afrane[3] list a number of such publications including experimental, theoretical, and modeling approaches.

Among the interesting dilute near-critical state phenomena, one can point out the peculiar dew point behavior that has come to be known[4] as double retrograde vaporization (DRV). This phenomenon was noticed experimentally by Chen et al.[5] for the system (methane + butane). Raeissi and Peters[6] present a list of other publications giving further experimental evidence of DRV. Attempts to simulate this phenomenon using equation of state methods have been pointed out by Raeissi and Peters.[7] Following nearly three decades of neglect, a new phenomenological interest in DRV has emerged. Raeissi and Peters[8] have given explanations of the behavior and the transitions involved in both *P,x,y* and *P,T* coordinates. Deiters[9] validated the phenomenon using classical thermodynamic relations. The starting point for his investigation was the Gibbs-Konowalow equation, which can be regarded as the generalizations of the Clapeyron equation for mixtures. Using this equation, the slope of the isothermal pressure−composition relation at coexistence is related to volumetric properties. The conditions of DRV require that $dP/dx|_{CXC} = \infty$ at three different points on the *P,x*

diagram. Using the above-mentioned equation, the criterion of DRV is simplified into the requirement of the intersection of two volumetric curves: the *volume slope curve*, which represents the volume and composition differences between coexisting phases as a function of pressure, and the *partial molar volume curve*, which represents the difference of the molar volume of the vapor phase and the partial molar volume of the solute as a function of pressure.[9] At this stage, Deiters used a series expansion of the molar Helmholtz energy as the tool to come to this DRV requirement.

In this study, we have attempted to further verify DRV by going deeper into the underlying infinite-dilution critical phenomena and highlighting the clashes between infinite-dilution versus critical behavior. It is shown that it is exactly this disagreement between the infinite-dilute and critical states in asymmetrical systems that is responsible for producing the typical behavior distinctive of DRV.

Theory

Double retrograde vaporization is a phenomenon characterized by an unexpected retrograde dew point curve at compositions approaching nearly pure volatile component and at temperatures very close to the critical temperature of the more volatile component. It is believed that all mixtures with a high degree of asymmetry (difference in size, shape, and energy between the solute and solvent molecules) will exhibit DRV behavior.[7,8]

Let us denote solvent and solute with subscripts 1 and 2, respectively. On the pressure−solubility diagram, instead of the single-domed dew point curve in the familiar "single" retrograde vaporization, DRV shows two "domes" at temperatures above but close to T_{c1} (Figure 1). At temperatures below but close to T_{c1}, the dew point curve has an inverse "S" shape. These result, respectively, in quadruple- or triple-valued dew points at a specific composition. DRV occurs within a very limited composition and temperature range, close to the critical point of the more volatile component. It is the result of the continuous phase transition from the critical point of pure volatile component to the critical point of the mixture, very highly concentrated with the more volatile component. Detailed explanations of this behavior and the transitions involved are given elsewhere.[8]

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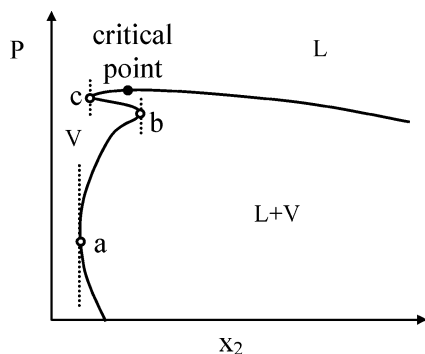
Figure 1. Schematic presentation of double retrograde vaporization on *P,x* coordinates at a temperature higher than the solvent's critical temperature.
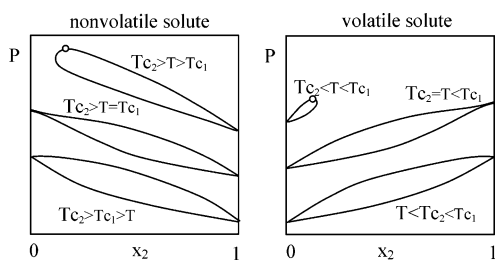

Figure 2. Schematic presentations of liquid−vapor phase behavior of a nonvolatile solute (left) and a volatile solute (right) at different temperatures.

If we define "solute" as the component with the lowest concentration in the mixture, then the discussion of DRV only makes sense when the solute is less volatile than the solvent. This is shown in the isothermal pressure−composition diagrams of Figure 2 for the two cases of nonvolatile (left) and volatile (right) solutes. All throughout this text, the words volatile and nonvolatile only indicate the relative volatility of solute to solvent, i.e., nonvolatile is used whenever the solute is less volatile than the solvent. In the case of nonvolatile solute, as long as $T < T_{c2}$, both the sub- and supercritical dew-bubble curves stretch all the way to the $x_2 = 1$ axis. However, with volatile solutes, dew-bubble loops shrink to a point at the critical temperature of the solvent.[2]

For a binary mixture, the slopes of the P,T,x equilibrium surfaces are given by the Gibbs-Konowalow equations. For the dew point surface, in a direction perpendicular to the T axis, the equation can be written as:[10]

$$\left(\frac{\partial P}{\partial x_2}\right)^V_{T,CXC} = \frac{\left(\frac{\partial^2 G}{\partial x_2{}^2}\right)^V_{T,P}}{\frac{V^L - V^V}{x_2^L - x_2^V} - \left(\frac{\partial V}{\partial x_2}\right)^V_{T,P}} \quad (1)$$

The superscripts V and L denote the vapor and liquid phases, respectively, and CXC symbolizes the coexistence surface of the two phases.

The condition of DRV requires three points of infinite slope on the isothermal P,x diagram (points *a*, *b*, and *c* in Figure 1), satisfying the condition $(\partial P/\partial x_2)^V_{T,CXC} = \infty$. According to eq 1, this can arise from either an infinite value of $(\partial^2 G/\partial x_2^2)^V_{T,P}$ or a zero value of $(V^L - V^V)/(x_2^L - x_2^V) - (\partial V/\partial x_2)^V_{T,P}$.

First let us consider the values of $(\partial^2 G/\partial x_2^2)^V_{T,P}$. As a result of the principle of minimal Gibbs energy: $(\partial^2 G/\partial x_2^2)^V_{T,P} \geq 0$, being equal to zero at the mixture critical point, and having a finite positive value at all other conditions except $x_2 = 1$ or 0.
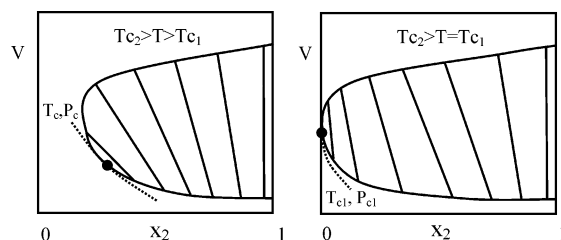

Figure 3. Molar volume versus composition of solute. The figure on the left is at a temperature above and the one on the right at the critical temperature of the solvent.

However, when treating a very dilute mixture, one has to pay attention to the peculiar behavior at the critical point of the system. This can be explained more easily in terms of osmotic susceptibilities. By definition:

$$\left(\frac{\partial^2 G}{\partial x_2^2}\right)_{T,P} = \frac{1}{x_1}\left(\frac{\partial \mu_2}{\partial x_2}\right)_{T,P} \quad (2)$$

in which $(\partial x_2/\partial \mu_2)_{T,P}$ is the osmotic susceptibility. It is known that the osmotic susceptibility diverges along the critical line. This is in agreement with $(\partial^2 G/\partial x_2^2)^V_{T,P} = 0$ at the critical point, as stated above. However, it has been shown by Levelt Sengers[2,11] that in this respect, dilute mixtures experience a serious dilemma. She has theoretically shown that the osmotic susceptibility of a dilute mixture $(\partial x_2/\partial \mu_2)_{T,P}$ behaves as x_2/RT, approaching zero, as it should at infinite dilution. So it is clear that a dilute mixture in the vicinity of a critical point is subjected to conflicting conditions of the osmotic susceptibility: approaching zero because of diluteness, and approaching infinity because of criticality.

In the general case of DRV, the mixture approaches infinite dilution, not necessarily reaching the point of $x_2 = 0$. So the osmotic susceptibility can approach values close to zero, but not zero itself. Hence, it is not possible for $(\partial^2 G/\partial x_2^2)^V_{T,P}$ to become infinite as long as the solute has a finite concentration. Thus, in general, the term $(\partial^2 G/\partial x_2^2)^V_{T,P}$ in eq 1 cannot be responsible for an infinite value of $(\partial P/\partial x_2)^V_{T,CXC}$.

The focus of DRV must therefore be directed to conditions that satisfy:

$$\frac{V^L - V^V}{x_2^L - x_2^V} - \left(\frac{\partial V}{\partial x_2}\right)^V_{T,P} = 0 \quad (3)$$

The value of $(V^L - V^V)/(x_2^L - x_2^V)$ is actually the slope of tie lines on an isothermal $V - x$ diagram, such as shown in Figure 3 for the case of a nonvolatile solute dissolved in a volatile solvent. The solid curve indicates the coexistence boundary, the straight lines are tie lines of constant pressure, and the filled circle is the mixture critical point. The left figure shows the phase behavior at a temperature above that of the pure solvent critical temperature, T_{c1}. However, as the temperature is lowered to that of T_{c1}, the coexistence curve has its extremum at the x_1 axis as shown in the figure on the right. Naturally, the tie lines approach a vertical slope as the system approaches pure solvent.

To investigate the conditions at which eq 3 is satisfied, one can consider an isothermal mixture of constant composition and increase pressure up to the critical point of the mixture. In this case, it is necessary to know the relationship of the tie lines of Figure 3 to pressure. As will be shown, we are confronted with the dilemma of contradicting behavior at infinite dilution versus critical conditions.

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In general, for a near-critical mixture, scaling laws suggest that on a path of constant temperature to the mixture critical point:[12]

$$x_2^L - x_2^V \propto (P_c - P)^\beta \text{ at } T = T_{cm} \tag{4}$$

where β is the critical exponent with a classical (analytic) value of $1/2$; nonclassical theories predict a value of approximately 0.33. However, Bischoff and Rosenbauer[13] obtained some precise data on dilute systems of NaCl−H$_2$O near the critical temperature of water, which indicated an effective critical exponent greater than the values of β predicted by any theory, classical or nonclassical.

Harvey and Levelt Sengers[12] showed that the classical expansion of the Helmholtz energy about the solvent's critical point leads to a scaling relationship at the solvent's critical temperature as infinite dilution is approached, given by

$$x_2^L - x_2^V \propto (P_c - P)^{\beta+1} \quad \text{at } T = T_{c1} \tag{5}$$

with a classical exponent of $\beta + 1 = 3/2$. Nonclassical analysis of the limiting behavior, for example, with the Leung-Griffiths model, shows that the characteristic exponent is indeed $\beta + 1$, in this case equal to 1.33. While this result is strictly valid only at $T = T_{c1}$, the influence of the solvent critical point persists in nearby regions. Therefore a dilute near-critical mixture goes through a region of competition between the $\beta + 1$ and β exponents as the critical point of pure solvent is approached.[14]

However, this particular shift in exponents is only particular to the P,x analysis. In P,ρ coordinates, whether infinitely dilute or critical, the characteristic exponent is always β (Harvey and Levelt Sengers[12]):

$$\rho^L - \rho^V \propto (P_c - P)^\beta \tag{6}$$

This equation is asymptotically valid for a pure fluid as it approaches its critical point and for a mixture if its critical point is approached at constant temperature. Since a linear variation in V is asymptotically equivalent to a linear variation in density, then

$$V^L - V^V \propto -(P_c - P)^\beta \tag{7}$$

The slopes of tie lines on an isothermal V,x diagram behave as

$$\frac{V^L - V^V}{x_2^L - x_2^V} \propto -\frac{(P_c - P)^\beta}{(P_c - P)^\beta} = -\text{ const.}$$
$$\text{near the mixture critical point at } T = T_{cm} \tag{8}$$

$$\frac{V^L - V^V}{x_2^L - x_2^V} \propto -\frac{(P_c - P)^\beta}{(P_c - P)^{\beta+1}} = -\frac{\text{const.}}{(P_c - P)}$$
$$\text{approaching infinite dilution at } T = T_{c1} \tag{9}$$

Although eq 9 strictly holds at the critical temperature of pure solvent, resulting in tie lines of diverging slope, its effect is also seen in closely neighboring regions, as phase behavior transitions do not go through abrupt breaks, but rather, through continuous changes. Therefore, a plot of $(V^L - V^V)/(x_2^L - x_2^V)$ as a function of pressure for a very dilute mixture (Figure 4) would produce a very steep, but nondiverging minimum in the vicinity of the solvent's critical pressure. The curve must then return to end at the mixture critical point at a finite constant value according to eq 8. At the other concentration extreme
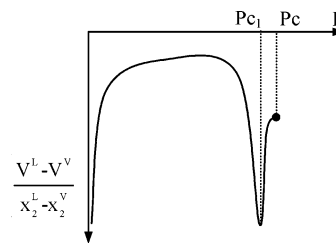

Figure 4. Schematic presentation of a very dilute mixture at a temperature slightly above the solvent's critical temperature.

approaching pure solute, by going down in pressure to the saturation pressure of the solute, again the $(V^L - V^V)/(x_2^L - x_2^V)$ curve starts to diverge since V,x tie lines have to become vertical as pure solute conditions are approached.

Now, let us consider the behavior of $(\partial V/\partial x_2)_{T,P}$ as a function of pressure by looking back at the diagram on the left side of Figure 3. An isothermal−isobaric curve at the critical temperature and pressure of the mixture is also plotted on this figure as a dashed curve. At the mixture critical point, the isothermal−isobaric curve is tangent to the coexistence curve. At this limiting point, the tie lines also approach the same slope as the coexistence curve and the isotherm−isobar, hence:

$$\left(\frac{\partial V^V}{\partial x_2}\right)^c_{T,P} = \left(\frac{V^L - V^V}{x_2^L - x_2^V}\right)^c \tag{10}$$

In this equation, the superscript c indicates critical. As the temperature is decreased to that of the critical temperature of the pure solvent, the tangent to the critical point goes from finite to infinite slope (Figure 3, right). As a consequence, $(\partial V/\partial x_2)_{T,P}$, which is finite at other critical points, diverges at the pure solvent critical point.[11] This can be formulated by noting that

$$\left(\frac{\partial V}{\partial x}\right)_{T,P} = -\left(\frac{\partial V}{\partial P}\right)_{T,x}\left(\frac{\partial P}{\partial x}\right)_{V,T} = V\kappa_{Tx}\left(\frac{\partial P}{\partial x}\right)_{V,T} \tag{11}$$

where κ_{Tx} is the isothermal compressibility of the fluid mixture. For the limit where the solvent's critical point is approached, Krichevskii[15] has shown that the value of $(\partial P/\partial x)_{V,T}$ can be related to the slope of the vapor pressure curve of the pure solvent at the critical point $(dP/dT)^c_{CXC}$ and the initial slopes of the critical line, $(dP/dx_2)^c_{CRL}$ and $(dT/dx_2)^c_{CRL}$:

$$\lim_{x_2\to0}\left(\frac{\partial P}{\partial x_2}\right)^c_{V,T} = \left(\frac{dP}{dx_2}\right)^c_{CRL} - \left(\frac{dP}{dT}\right)^c_{CXC}\left(\frac{dT}{dx_2}\right)^c_{CRL} \tag{12}$$

The superscript c indicates that, at mole fraction $x_2 = 0$, the limiting value of the derivative is taken at the solvent's critical point. The quantity on the left-hand side of this equation, called the Krichevskii parameter,[2] has proven to be very important since it determines the dilute mixture behavior near the solvent's critical point, i.e., it is indicative of solute−solvent interactions at infinite dilution.

In the region around the solvent's critical point, if the limit $x_2 \to 0$ is taken first, the limit of $(\partial P/\partial x_2)_{V,T}$ is well-behaved and finite, so it is possible to approximate it by the value of the Krichevskii parameter.[11,16] However, in this same limit, κ_{Tx} approaches κ_T, the compressibility of the pure fluid, which is strongly divergent.[17] So even though in eq 11, $(\partial V/\partial x_2)_{T,P}$ is strictly defined as a function of the isothermal compressibility on a path of constant composition, if the limit $x_2 \to 0$ is taken first, this path restriction eases to a constant temperature path for a pure component and hence $(\partial V/\partial x_2)_{T,P}$ diverges simply as κ_T.
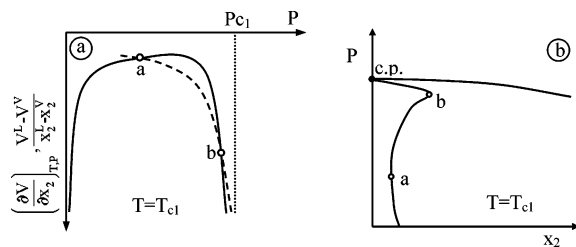
Figure 5. Schematic presentation of an infinitely dilute mixture at the solvent's critical temperature. The solid curve of (a) represents $(V^L - V^V)/(x_2^L - x_2^V)$, while the dashed curve shows $(\partial V/\partial x_2)_{T,P}$. The filled circle is the mixture's critical point.

Figure 6. Schematic presentation of a very dilute mixture at a temperature slightly above the solvent's critical point. The solid curve of (a) represents $(V^L - V^V)/(x_2^L - x_2^V)$ while the dashed curve shows $(\partial V/\partial x_2)_{T,P}$. The filled circle is the mixture's critical point.
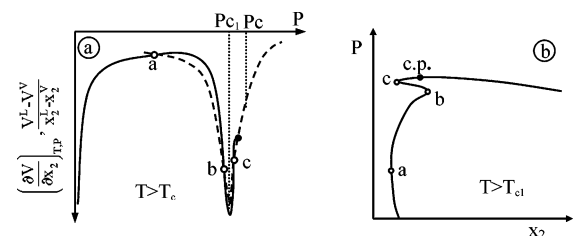
The pressure dependence of $(\partial V/\partial x_2)_{T,P}$ can then be investigated by considering the behavior of the solvent's compressibility. A scaling law established along a critical isotherm, is given by[18]

$$\kappa_T \propto (P_c - P)^{(1/\delta)-1} \quad \text{at } T = T_{c1} \tag{13}$$

Here the classical exponent is $\delta = 3$, while nonclassically it has the value $\delta = 4.8$. According to eq 11, at infinite dilution $(\partial V/\partial x_2)_{T,P}$ and $V\kappa_T$ are related by the constant finite Krichevskii parameter. Hence, the relationships that are applicable to the isothermal compressibility can also be used for $(\partial V/\partial x_2)_{T,P}$:

$$\left(\frac{\partial V}{\partial x_2}\right)_{T,P} \propto (P_c - P)^{(1/\delta)-1} \quad \text{at } T = T_{c1} \tag{14}$$

since the Krichevskii parameter is negative for nonvolatile attractive solutes, the divergence is negative.

With the above information, it is possible to plot the two terms of eq 3. Consider an infinitely dilute mixture at a constant temperature of $T = T_{c1}$ and gradually increase the pressure up to P_{c1}, the critical pressure of the solvent. $(V^L - V^V)/(x_2^L - x_2^V)$ approaches infinity very sharply as $(P_c - P)^{-1}$ while $(\partial V/\partial x_2)_{T,P}$ goes to infinity more gradually as $(P_c - P)^{-2/3}$ in the classical case and $(P_c - P)^{-0.79}$ nonclassically. This can result in two intersections between $(V^L - V^V)/(x_2^L - x_2^V)$ and $(\partial V/\partial x_2)_{T,P}$ as shown in Figure 5a, corresponding to the minimum (point a) and maximum (point b) on the pressure–solubility curve (Figure 5b). Point a corresponds to the commonly occurring extrema indicative of retrograde condensation, which can occur even in systems that do not exhibit DRV.

By gradually increasing the temperature slightly above T_{c1} (Figure 6), $(V^L - V^V)/(x_2^L - x_2^V)$ and $(\partial V/\partial x_2)_{T,P}$ will start to lose their diverging nature. However, even though they will no longer have their limiting proportionalities to $(P_c - P)^{-1}$ and $(P_c - P)^{-2/3}$, they will still both go to very large but finite values at $P = P_{c1}$ and the curve of $(V^L - V^V)/(x_2^L - V_2^V)$ will still be more steep than $(\partial V/\partial x_2)_{T,P}$. Upon returning from the high peak at P_{c1}, the two curves meet at the mixture critical point (as
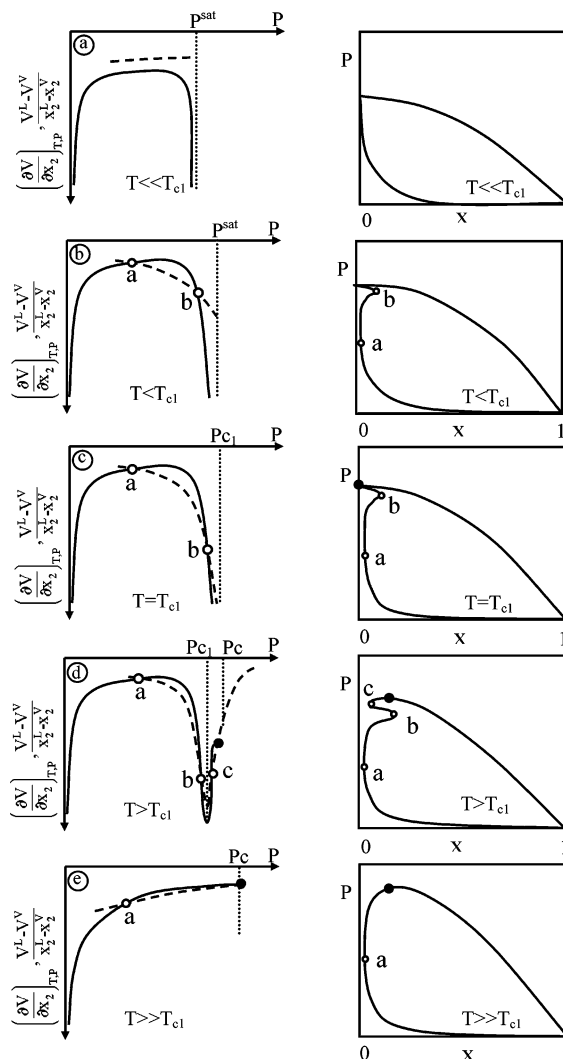

Figure 7. Schematic presentation of transitions of very dilute mixtures as temperature is increased from far below (figure a) to far above (figure e) the solvent's critical temperature. The solid curves on the left represent $(V^L - V^V)/(x_2^L - x_2^V)$ while the dashed curves show $(\partial V/\partial x_2)_{T,P}$. The filled circles are the mixtures' critical points.

discussed for the V,x graph and also in eq 10). This results in the additional intersection point "c" as shown in Figure 6a, corresponding to another minimum on the pressure solubility curve (Figure 6b).

All the transitions involved upon going from a low temperature far below, to a very high temperature, far above the critical temperature of pure solvent (T_{c1}) are schematically shown in Figure 7. At temperatures below T_{c1} (Figure 7a,b), the bubble and dew curves meet at the saturation pressure of pure solvent. V,x tie lines are vertical for a pure solvent, indicating a diverging value of $(V^L - V^V)/(x_2^L - x_2^V)$. If the temperature is far below T_{c1}, $(\partial V/\partial x_2)_{T,P}$ falls above $(V^L - V^V)/(x_2^L - x_2^V)$, and there is no intersection (Figure 7a), and thus no DRV behavior. However, when the temperature approaches very close to T_{c1}, $(\partial V/\partial x_2)_{T,P}$ starts to approach its diverging behavior, resulting in two intersection with $(V^L - V^V)/(x_2^L - x_2^V)$, indicative of the triple-valued double retrograde behavior at temperatures below T_{c1} (Figure 7b). As temperature gradually increases to pass T_{c1}, the slope of $(\partial V/\partial x_2)_{T,P}$ increases sharply to give the full double-domed dew point curve shown on the right side of Figure 7d. When the temperature is raised far above T_{c1} the diverging behavior of both $(\partial V/\partial x_2)_{T,P}$ and $(V^L - V^V)/(x_2^L - x_2^V)$ diminish,
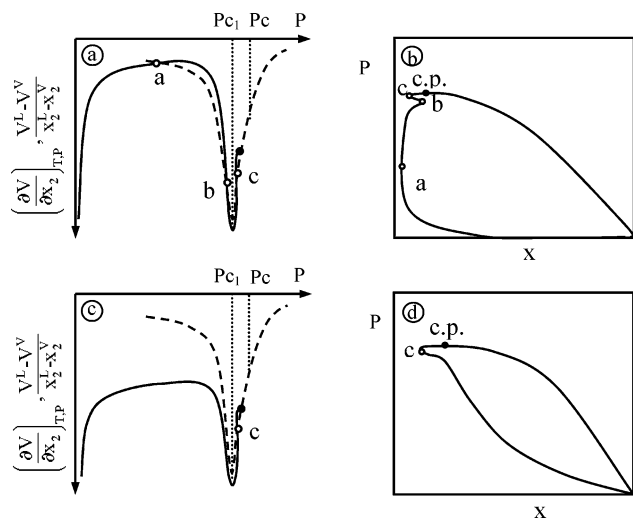
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Figure 8. Schematic presentations of dilute mixtures composed of an asymmetric solute−solvent pair (top) compared to a rather symmetric mixture (bottom). The solid curves of (a) and (c) represent $(V^L - V^V)/(x_2^L - x_2^V)$ while the dashed curves show $(\partial V/\partial x_2)_{T,P}$. The filled circles are the mixtures' critical points.

leaving two intersections as shown in Figure 7e, namely, point a and the critical point of the mixture itself.

The reasonings given here are general and apply to both classical and nonclassical fluids.

It was noted by Raeissi and Peters[7,8] that DRV can only occur in systems where the molecular asymmetry between solvent and solute is large enough to produce a very steep P,y dew point curve. This indicates that the three intersections of Figure 6a do not necessarily occur in all systems. Figure 8 shows the behavior of dilute mixtures of a very asymmetric solute−solvent pair (top) in comparison to a relatively similar solute−solvent pair (bottom). Solute−solvent pairs of similar molecules produce comparatively narrower phase envelopes with nonsteep dew point curves (Figure 8d). In such systems, vapor and liquid compositions do not differ as greatly. So $(V^L - V^V)/(x_2^L - x_2^V)$ takes larger negative values (Figure 8c), while the values of $(\partial V/\partial x_2)_{T,P}$ are more or less similar to greatly asymmetric solvent−solute pairs. Therefore, these two curves may no longer cross one another as shown in Figure 8c. For DRV to occur, the crossing of these two curves must happen *before* reaching their minima. These minima are obviously at the critical pressure of the solvent; for example, the minimum of $(\partial V/\partial x_2)_{T,P}$ occurs at the point where the isothermal compressibility of the pure solvent reaches a maximum, which is of course at P_{c1}. The criteria for the existence of DRV can therefore be indicated as having enough asymmetry between solvent and solute to produce the following condition at a pressure range (or at least at one pressure for DRV to begin) smaller than the critical pressure of the pure solvent:

$$\left(\frac{\partial V}{\partial x_2}\right)_{T,P} < \frac{V^L - V^V}{x_2^L - x_2^V} \quad \text{at } P < P_{c1} \tag{15}$$

Or alternatively, by writing the Gibbs-Konowalow equation perpendicular to the P axis:[10]

$$\left(\frac{\partial T}{\partial x_2}\right)_{P,CXC}^V = -\frac{\left(\dfrac{\partial^2 G}{\partial x_2^2}\right)_{T,P}^V T}{\dfrac{H^L - H^V}{x_2^L - x_2^V} - \left(\dfrac{\partial H}{\partial x_2}\right)_{T,P}^V} \tag{16}$$

And carrying out the same procedure as above, one can obtain the enthalpy-based DRV criteria as follows:

$$\left(\frac{\partial H}{\partial x_2}\right)_{T,P} < \frac{H^L - H^V}{x_2^L - x_2^V} \quad \text{at } P < P_{c1} \tag{17}$$

It is interesting to note that one can retrieve the P,x coordinate criteria of DRV by replacing eq 15 into eq 1:

$$\frac{\left(\dfrac{\partial^2 G}{\partial x_2^2}\right)_{T,P}^V}{\left(\dfrac{\partial P}{\partial x_2}\right)_{T,CXC}^V} > 0 \quad \text{at } P < P_{c1} \tag{18}$$

Since $(\partial^2 G/\partial x_2^2)_{T,P}^V$ cannot be negative, this is equivalent to saying that there must exist at least one pressure below the critical pressure of pure solvent for which the dew point curve exhibits a positive slope on the pressure−solubility diagram. This is of course the obvious distinction of DRV behavior.

One must note from the above that the intersection point c, however, can still occur for similar solute−solvent pairs, as shown in Figure 8c. This does not contradict DRV behavior.

It must also be noted that dilute mixtures of nonvolatile solutes in supercritical solvents always have negative solute partial molar volumes (Levelt Sengers[2]; Petsche and Debenedetti[19]). This is in conflict with Deiters' reasoning[9] that strongly repulsive solutes will also result in DRV, but with signs of $(V^L - V^V)/(x_2^L - x_2^V)$ and $(\partial V/\partial x_2)_{T,P}$, opposite to those discussed in previous sections. As mentioned previously, DRV only makes sense for systems of nonvolatile solutes in volatile solvents. Such systems only have negative solute partial molar volumes, and so the opposite signed values of $(V^L - V^V)/(x_2^L - x_2^V)$ and $(\partial V/\partial x_2)_{T,P}$, as proposed by Deiters are not possible.

Conclusions

Thermodynamic formulations of critical phenomena have been used to explain the occurrence of triple- or quadruple-valued dew points, characteristic of DRV. It is possible to translate DRV into the volumetric properties of the two phases, namely, differential molar volumes and the slopes of tie lines on the V,x diagram. These properties behave differently at conditions of infinite dilution as compared to critical. Once the two conditions approach one another, the behavior dictated by infinite dilution can clash with that of near-critical. This conflict is the element responsible for producing DRV. It is therefore only obvious that these same volumetric terms can be used as a measuring tool to determine the limits at which DRV starts to form. The reasoning given indicates that double retrograde behavior is a general phenomenon and occurs in any system in which the nonvolatile solute molecules have a high degree of asymmetry with respect to the solvent molecules.

Nomeclature

G	molar Gibbs free energy
H	molar enthalpy
P	pressure
P_c	critical pressure
T	temperature
T_c	critical temperature
V	molar volume
x	mole fraction
β	critical exponent

δ	critical exponent
κ_{Tx}	isothermal compressibility of mixture
μ	chemical potential
ρ	molar density

Subscripts

1	solvent
2	solute
CXC	coexistence
CRL	critical line
m	mixture

Superscripts

c	critical
L	liquid
V	vapor

References and Notes

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