Tricitical and Critical-End-Point Behavior of Interfacial Tensions in Fluid Mixtures

Ian L. Pegg,[(a)] M. Cynthia Goh, Robert L. Scott, and Charles M. Knobler

Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90024

(Received 5 August 1985)

Interfacial tensions σ in the tricritical region of mixtures of ethane with higher alkanes were measured by surface light scattering. At each of the two critical end points σ for the noncritical interface shows the predicted behavior: σ and $d\sigma/dT$ appear continuous while $d^2\sigma/dT^2$ changes sign. Results for the $\alpha\gamma$ interface suggest high adsorption. The tricritical exponent for σ varies across the three-phase region and appropriate ratios of σ do not approach unity, in disagreement with a van der Waals–type theory of interfaces.

PACS numbers: 64.60.Kw, 64.60.Fr, 68.10.Cr

In this Letter we describe an experimental test of recent theoretical predictions concerning the behavior of the interfacial tensions σ of fluid mixtures in the vicinity of a tricritical point. Our measurements of σ across critical and noncritical boundaries between two- and three-phase regions are in good agreement with theory. The situation concerning the behavior in a direction towards the tricritical point is less clear, however, and a number of discrepancies between theory and experiment are evident, the most notable of which is an asymmetry that seems to persist as the tricritical point is approached.

In fluid mixtures tricritical phenomena are associated with regions of three-phase coexistence bounded by critical end points. At one end point two of the phases, say α and β, become identical in the presence of the γ phase, while at the other end point β and γ become identical in the presence of α.

We will assume, as observed in our system, that β perfectly wets the $\alpha\gamma$ interface and therefore $\sigma_{\alpha\gamma}=\sigma_{\alpha\beta}+\sigma_{\beta\gamma}$. Widom[1] has used the one-density square-gradient theory of interfaces to study the behavior of σ along a path of changing temperature and fixed composition through a critical end point with the result that, for the noncritical interface,

$$\sigma=\sigma_{\text{cep}}+a(T-T_{\text{cep}})+b(T-T_{\text{cep}})^{\mu}+\ldots, \quad (1)$$

where $T-T_{\text{cep}}$ is the difference in temperature from its value at the critical end point (cep) and $\mu=1.26$ is the surface-tension critical exponent. The coefficient a is found to be the same in the two- and three-phase regions, implying a common tangency at T_{cep} of $\sigma_{\alpha\gamma}$ and $\sigma_{\alpha\beta}$ in the three-phase region with $\sigma_{\alpha,\beta\gamma}$ in the two-phase region (and of $\sigma_{\alpha\gamma}$ and $\sigma_{\beta\gamma}$ with $\sigma_{\alpha\beta,\gamma}$ at the other critical end point); b changes magnitude and sign at T_{cep}.

Robert and Tavan[2] have proved that for such a path σ and $d\sigma/dT$ obtained from the square-gradient theory are continuous at a cep for any number of phases and densities and Telo da Gama, Evans, and Hadjiagapiou[3] reached similar conclusions from numerical calculations on a two-density theory that was not based on the square-gradient approximation. Recently Lazenby and Rudnick[4] have obtained (1) from a renormalization-group calculation. Previous experimental studies,[5] however, have proved much less conclusive, but our new results lend strong support to (1).

We consider next a path with changing temperature from the $\alpha\gamma$ two-phase region into the three-phase region along which β appears as a bulk phase via a first-order transition. Cahn[6] has given a rather general treatment of this situation in which α or γ may equally well be solid. For our purpose his important conclusion is that when $\sigma_{\alpha\gamma}=\sigma_{\alpha\beta}+\sigma_{\beta\gamma}$ holds in the three-phase region, the $\alpha\gamma$ interface in the two-phase region is structured to consist of a microscopic layer of β whose thickness diverges as $\ln|T-T_s|$, where T_s is the temperature at the boundary of the three-phase region where β becomes a stable bulk phase. The resulting logarithmic divergence in the adsorption implies a logarithmic divergence in $d\sigma/dT$ at fixed composition. Our results are in qualitative agreement with this previously unverified prediction.

Ternary mixtures of ethane with normal hydrocarbons in the C_{16}–C_{20} range have limited three-phase regions at temperatures and pressures close to the critical point of ethane. The mixtures are quasibinary[7–9]; that is, to a good approximation they can be treated as a binary mixture of ethane with a solute characterized by the mole-fraction-average carbon number $\langle n\rangle$ of the higher-molecular-weight alkanes. The width of the three-phase region, as measured by the difference of the upper and lower critical-end-point temperatures $\Delta T=T_{\text{ucep}}-T_{\text{lcep}}$, vanishes at the tricritical point and obeys the asymptotic scaling $\Delta T\sim(\Delta n)^{3/2}=(\langle n\rangle-n_t)^{3/2}$, with n_t close to 17.6. Thus, the approach to the tricritical point can be investigated by studying mixtures with different values of $\langle n\rangle$. For a given mixture the three-phase region can be traversed by simply changing the temperature and, depending on the proportion of ethane, the transition to a two-phase region can occur either by the merging of two phases at a critical end point or by the disappearance of one phase. Since we determine ΔT with greater precision than Δn we use $(\Delta T)^{2/3}$ as our measure of the distance from the tricritical point.

The quasibinary system ethane + (n-octadecane + n-nonadecane) was chosen for this study because the interfacial tensions are sufficiently large to be measured with high precision by analyzing the spectrum of light scattered from thermal capillary waves.[10-12] Light ($\lambda = 632.8$ nm) incident on an interface at close to the critical angle was scattered and mixed with a local oscillator provided by a diffraction grating[12] positioned in the beam and imaged onto the interface with a lens system. The correlation functions were fitted with the numerical Fourier transform of the (broadened) theoretical power spectrum[11] with an appropriate dispersion relation.[13] We determine the quantity $\sigma + g\Delta\rho/q^2$, where g is the acceleration of gravity, $\Delta\rho$ is the difference of the mass densities of the two bulk phases, and q is the scattering vector. Under the conditions of large q used, the gravitational term is usually small. The analysis requires knowledge of the densities of both bulk phases, but is much more sensitive to the sum than to the difference. The densities in the three-phase region are known[8]; along paths into two-phase region we used the values at the phase boundary.

Figure 1 shows our results for the binary system with $\langle n \rangle = 18$ for which $\Delta T = 0.166$ K. The measurements along the lines A and B, which were obtained on samples in which the ethane content was carefully adjusted to make the meniscus appear at the center of the critical phase, suggest that $d\sigma/dT$ is indeed continuous at the cep's. However, a discontinuity develops quickly when the density is slightly off critical. Measurements made on samples with T_s imperceptibly different from T_{cep}, but where the meniscus vanished above or below the center of the critical phase, showed definite discontinuities in $d\sigma/dT$ while that in σ itself (proportional to $|T_{\mathrm{cep}} - T_s|^{\mu}$) was undetectable.

Since each interfacial tension is required to vanish at its respective critical point as $|T - T_c|^{\mu}$, we have analyzed our results not in terms of (1) but rather with

$$\sigma = C|T - T_c|^{\mu}[1 + A(T - T_{\mathrm{cep}}) + B|T - T_{\mathrm{cep}}|^{\mu}], \tag{2}$$

where A, B, and C are constants (for fixed $\langle n \rangle$) and as before $\mu = 1.26$. The curvature in the three-phase region is dominated by the vanishing of σ and thus the fits in Fig. 1 correspond to (2) with $B = 0$ in the three-phase region; allowing a nonzero B there had little effect. Recently Lazenby and Rudnick[4] have found that inclusion of a capillary-wave contribution in their renormalization-group calculation of σ gives rise to a $|T - T_{\mathrm{cep}}|^{\beta}$ term ($\beta = 0.32$) in the three-phase region and a concomitant infinity in $d\sigma/dT$ at T_{cep}; our measurements suggest that if this term is present its amplitude is small.

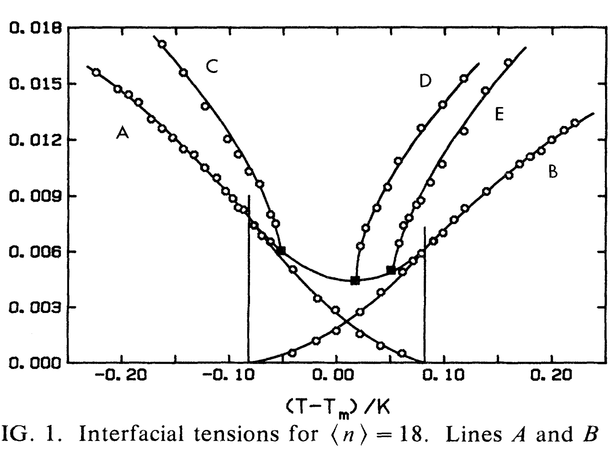

FIG. 1. Interfacial tensions for $\langle n \rangle = 18$. Lines A and B result from the fitting of the data for $\sigma_{\alpha\beta}$ and $\sigma_{\beta\gamma}$, respectively, by Eq. (2); their sum in the three-phase region is $\sigma_{\alpha\gamma}$. Other lines are simply to guide the eye.

We turn now to the interfacial tensions in the $\alpha\gamma$ two-phase region for three off-critical loadings (curves C, D, and E). In each of these samples the bulk β phase appears ($T = T_s$) as a thin (~ 0.3 mm) layer when the temperature is either increased (C) or decreased (D and E) and grows quickly when the temperature is changed further. T_s was determined for each curve and since $\sigma_{\alpha\gamma} = \sigma_{\alpha\beta} + \sigma_{\beta\gamma}$ we can obtain $\sigma_{\alpha\gamma}$ at the phase boundary from curves A and B. While values of T_s proved more difficult to determine than T_{cep} they were reproducible to ± 1 mK, and so we are convinced that the observed increasing and probably infinite slope is real.

As T_s was approached from the two-phase side we found a small but systematic worsening of the fits to the measured correlation functions; we believe this to be due to the diverging thickness of the adsorbed β-like layer. To examine this further we made similar measurments on the $C_2 + C_{19}$ system, which has a larger ΔT ($= 1.292$ K). The interfacial tensions $\sigma_{\alpha\beta}$ and $\sigma_{\beta\gamma}$ can then be sufficiently different to give two well-separated peaks in the power spectrum when β is present as a thin but visible layer. As T_s was approached from the two-phase side we observed in addition to a signal at high frequency, corresponding to the relatively large $\sigma_{\alpha\gamma} \approx \sigma_{\alpha\beta}$, a strong overdamped signal that moved out to higher frequencies and eventually corresponded to $\sigma_{\beta\gamma}$ above T_s. While we have observed these features as far as 15 mK from T_s, the first appearance of the β phase was more difficult to determine than in the $\langle n \rangle = 18$ system; because ΔT is larger the volume of this phase grows more slowly with temperature. We estimate an uncertainty in T_s of ± 5 mK here, and so we can conclude only that our results are suggestive of a microscopic β-like phase in the bulk two-phase region.

We have made measurements of $\sigma_{\alpha\beta}$ and $\sigma_{\beta\gamma}$ in the three-phase regions of four samples with $\langle n \rangle$ between 18 and 19. In all cases we obtain excellent fits to the

TABLE I. Parameters for Eq. (2) (with $B=0$) obtained from fits to data from the three-phase region. The constants C, A, and B have units appropriate to σ in millinewtons per meter and T in kelvins.

$\langle n \rangle$	ΔT (mK)	$C_{\alpha\beta}$	$A_{\alpha\beta}$	$C_{\beta\gamma}$	$A_{\beta\gamma}$
19	1292	0.0750(7)	−0.16(1)	0.0600(6)	0.21(2)
18.835	1106	0.0753(8)	−0.20(2)	0.0596(4)	0.26(1)
18.391	545	0.0772(6)	−0.39(4)	0.0643(8)	0.60(6)
18	166	0.076(2)	−2.5(3)	0.0621(9)	4.1(2)
18[a]	166	0.0753(5)	−2.5(2)	0.0603(5)	3.8(1)

[a] Fits for this line include two-phase data for $\sigma_{\alpha\beta}$ with $B = -5.1(3)$ and two-phase data for $\sigma_{\beta\gamma}$ with $B = -7.0(3)$.

TABLE II. Ratios referred to in the text. r_l and r_ξ refer to Eq. (5) with the susceptibilities measured by the scattered intensity or the square of the correlation length, respectively, from Kumar *et al.* (Ref. 20).

$\langle n \rangle$	$\dfrac{\sigma_{\alpha\beta}(\theta=-1)}{\sigma_{\beta\gamma}(\theta=1)}$	$\sigma_{\alpha\beta}/\sigma_{\beta\gamma}$	At $\theta=0$ r_l	r_ξ
19	1.21(2)	1.31(3)	2.2(2)	
18.8354	1.28(2)	1.33(3)		
18.3905	1.22(3)	1.31(5)		
18.1761			2.2(2)	1.5(8)
18	1.25(4)	1.46(8)	1.7(1)	1.3(2)
17.8752			2.0(2)	1.5(3)
17.7648			2.1(2)	1.6(3)

data using (2) with $B=0$ and the parameters given in Table I. However, we see a number of discrepancies between our measurements and a classical theory of the tricritical region and we therefore summarize some of the pertinent features of such a treatment.

Lang, Lim, and Widom[14] have used the one-density square-gradient theory of interfaces to obtain the interfacial tensions near a tricritical point. Their calculation is based on a sixth-order polynomial for the free energy,[15] the simplest expression that yields tricritical behavior. We have recently shown[16] that this asymptotic expression for the free energy does not account adequately for the observed thermodynamic properties of a number of systems and that higher-order terms must be included. Thus we have extended the theory of Lang, Lim, and Widom by using an eighth-order polynomial[17]; the result is

$$\sigma_{\alpha\beta} = Ig(\theta)(\Delta\zeta)^2 - Jh(\theta)(\Delta\zeta)^{5/2} + Kg(\theta)(\Delta\zeta)^3 - \dots, \tag{3a}$$

$$\sigma_{\beta\gamma} = Ig(-\theta)(\Delta\zeta)^2 + Jh(-\theta)(\Delta\zeta)^{5/2} + Kg(-\theta)(\Delta\zeta)^3 \dots, \tag{3b}$$

where I, J, and K are constants, $g(\theta)$ and $h(\theta)$ are functions, and $\Delta\zeta$ is the difference in a field variable ζ from its value at the tricritical point. [In our quasibinary systems $\Delta\zeta$ is approximately proportional to Δn or to $T_t - T_m$, where $T_m = (T_{\mathrm{ucep}} + T_{\mathrm{lcep}})/2$ is the midtemperature of the three-phase region.] The variable $\theta = 2(T-T_m)/\Delta T$ shows the relative position in the three-phase region and ranges from -1 at the lcep to $+1$ at the ucep. [For $J=K=0$, (3) reduces to equations that are equivalent to those of Lang, Lim, and Widom.] Thus, for fixed θ, $\sigma \sim (\Delta\zeta)^2$ asymptotically and therefore the tricritical exponent $\mu_t = 2$, a result previously derived[18] and confirmed by experiment[19] for the special case of $^3\mathrm{He} + {}^4\mathrm{He}$, a *symmetrical* (i.e., $\theta = 0$) tricritical system.

A feature of the original theory is the equality of $\sigma_{\alpha\beta}(\theta)$ and $\sigma_{\beta\gamma}(-\theta)$, a symmetry shown only asymptotically by (3). Lang, Lim, and Widom found their data on a quaternary three-phase system to be "in qualitative accord" with their asymptotic theory. Equation (3) implies that

$$\sigma_{\alpha\beta}(\theta)/\sigma_{\beta\gamma}(-\theta) - 1 \sim (\Delta n)^{1/2} \sim (\Delta T)^{1/3}.$$

Table II shows values of $\sigma_{\alpha\beta}(\theta)/\sigma_{\beta\gamma}(-\theta)$ obtained from our data; they show no sign of approaching unity while $(\Delta T)^{1/3}$ changes by a factor of 2. Indeed, within experimental error there is no dependence upon ΔT at all.

At each fixed value of θ we have examined the dependence of $\sigma_{\alpha\beta}$ and $\sigma_{\beta\gamma}$ on $\Delta\zeta \approx \Delta N$ measured by $(\Delta T)^{2/3}$. Classical theory, i.e. (3), predicts that in the asymptotic limit the slope s obtained from log-log plots of σ vs ΔT should be $\frac{2}{3}\mu_t = \frac{4}{3}$. However, we find that, for each interface, s shows a systematic dependence upon θ, rising monotonically from a value near 1.26 at the noncritical interface near the cep ($\theta = \pm 1$) to around 1.4 near the other cep ($\theta = \mp 1$, where this interface becomes critical); there is increasing curvature as the effective slope increases. These apparent increases as one goes from one cep to the other are largely a result of the σ's at $\langle n \rangle = 18$, and so we plan to investigate this effect with further experiments.

These results for the slope s are already evident in our fits with (2). If the identities $T - T_c = \Delta T(\theta \pm 1)/2$ and $T - T_{\mathrm{cep}} = \Delta T(\theta \mp 1)/2$ are substituted into (2), with $B=0$, one obtains

$$\sigma = C(\Delta T)^{\mu} |(\theta \pm 1)/2|^{\mu} [1 + (A/2)(\Delta T)(\theta \mp 1)]. \tag{4}$$

For σ to satisfy the proper tricritical scaling and be asymptotically proportional to $(\Delta T)^{4/3}$, C should be proportional to $(\Delta T)^{4/3-\mu} = (\Delta T)^{0.07}$ while A should be proportional to $(\Delta T)^{-1}$ or to a less negative power of ΔT. Table I shows the ΔT dependence of the fitted parameters; both C's are remarkably constant and both A's are roughly proportional to $(\Delta T)^{-1.3}$. If these features are incorporated into (4) and $s = (\partial \ln\sigma / \partial \ln\Delta T)_\theta$ determined, we get the same variation with θ seen in the log-log plots. We anticipate that a consistent nonclassical theory of critical-tricritical crossover may show differences between paths at different constant θ's. [An aspect of this crossover that arises even in a classical theory is clearly seen in our results: σ on paths of constant $\tau = T - T_m$ (τ is rougly proportional to the a_3 of Griffiths[15]) exhibits effective exponents that change smoothly from μ_t for $\tau = 0$ (the only path that passes through the tricritical point) towards μ as $|\tau|$ increases.]

It is possible that the discrepancies between our interfacial tensions and theory, notably the constant asymmetry implied by the ratios in Table II, reflect a breakdown of the square-gradient and/or the one-density approximations made in obtaining (3). We think that this is unlikely, particularly in view of the success of (1), since these approximations are expected to be reliable near a tricritical point,[21] the former as a result of the necessarily thick interfaces near critical points and the latter as a result of the asymptotically linear three-phase region in a space of densities.

Ramos-Gomez[22] has pointed out that a consequence of the *asymptotic* form of the free energy, that is, of the $(\Delta\zeta)^2$ term in (3), is the relation

$$\sigma_{\alpha\beta}/\sigma_{\beta\gamma} = (\chi_\alpha^{-1} - \chi_\beta^{-1})/(\chi_\gamma^{-1} - \chi_\beta^{-1}) = r, \qquad (5)$$

where χ_i is the susceptibility in phase i. In an extended classical treatment with higher-order terms in the free energy, such as gave (3), (5) is valid only in the asymptotic limit, but both ratios should approach the same value as $(\Delta T)^{1/3}$ decreases. The right-hand ratio r in (5) is accessible experimentally if one approximates the susceptibilities χ_i either by the intensities of light scattering I_i from the bulk phases or by the squares of the correlation lengths ξ. Table II compares, at the mid temperature T_m ($\theta = 0$), $\sigma_{\alpha\beta}/\sigma_{\beta\gamma}$ with r_I and r_ξ, taken from the experiments of Kumar *et al.*[20] Equation (5) predicts that for $\theta = 0$ r_I and r_ξ should approach unity as $(\Delta T)^{1/3}$, a prediction equivalent to that of (3) for $\sigma_{\alpha\beta}/\sigma_{\beta\gamma}$. Again this prediction is not borne out by experiment; each ratio is virtually constant.

Evidently this fundamental asymmetry extends to the susceptibilities in the bulk phases. We see no direct relation between this unexplained asymmetry and the nonclassical amplitude corrections[23] that Kumar *et al.*[20] have suggested as an explanation for the failure of the Griffiths sum rule[24] for the susceptibilities.

This research was supported by the National Science Foundation under Grants No. CHE81-00125, No. CHE82-10286, and No. CHE84-14463.

---

[a] Present address: Thermophysics Division, National Bureau of Standards, Gaithersburg, Md. 20899.

[1] B. Widom, J. Chem. Phys. **67**, 872 (1977); F. Ramos-Gomez and B. Widom, Physica (Amsterdam) **104A**, 595 (1980).

[2] M. Robert and P. Tavan, J. Chem. Phys. **78**, 2557 (1983).

[3] M. M. Telo da Gama, R. Evans, and I. Hadjiagapiou, Mol. Phys. **52**, 573 (1984).

[4] J. Lazenby and J. Rudnick, personal communication.

[5] N. Nagarajan, W. W. Webb, and B. Widom, J. Chem. Phys. **77**, 5771 (1982); I. L. Pegg, Ph.D. thesis, University of Sheffield, 1982 (unpublished).

[6] J. W. Cahn, J. Chem. Phys. **66**, 3667 (1977).

[7] J. Specovius, M. Leiva, R. L. Scott, and C. M. Knobler, J. Phys. Chem. **85**, 2313 (1981).

[8] M. C. Goh, J. Specovius, C. M. Knobler, and R. L. Scott, to be published.

[9] J. L. Creek, C. M. Knobler, and R. L. Scott, J. Chem. Phys. **74**, 3489 (1981).

[10] E. S. Wu and W. W. Webb, Phys. Rev. A **8**, 2077 (1973); J. Zollweg, G. Hawkins, and G. B. Benedek, Phys. Rev. Lett. **27**, 1182 (1971); I. A. McLure and I. L. Pegg, J. Mol. Struct. **80**, 393 (1982).

[11] M. A. Bouchiat and J. Meunier, J. Phys. (Paris), Colloq. **33**, C1-144 (1972).

[12] S. Hard, Y. Hamnerius, and O. Nilsson, J. Appl. Phys. **47**, 2433 (1976).

[13] M. Papoular, J. Phys. (Paris) **29**, 81 (1968); J. C. Herpin and J. Meunier, J. Phys. (Paris) **35**, 847 (1974).

[14] J. C. Lang, P. K. Lim, and B. Widom, J. Phys. Chem. **80**, 1719 (1976).

[15] R. B. Griffiths, J. Chem. Phys. **60**, 195 (1974).

[16] R. Lindh, I. L. Pegg, C. M. Knobler, and R. L. Scott, Phys. Rev. Lett. **52**, 839 (1984).

[17] R. L. Scott, to be published.

[18] M. Papoular, Phys. Fluids **17**, 1038 (1974); B. Widom, J. Chem. Phys. **62**, 1332 (1975).

[19] P. Leiderer, H. Poisel, and M. Wanner, J. Low Temp. Phys. **28**, 167 (1977).

[20] A. Kumar, R. Chamberlin, D. S. Cannell, I. L. Pegg, C. M. Knobler, and R. L. Scott, Phys. Rev. Lett. **54**, 2234 (1985).

[21] B. Widom, in *Statistical Mechanics and Statistical Methods in Theory and Application,* edited by U. Landman (Plenum, New York, 1977).

[22] F. Ramos-Gomez, J. Chem. Phys. **74**, 4737 (1981).

[23] M. E. Fisher and S. Sarbach, Phys. Rev. Lett. **41**, 1127 (1978).

[24] M. Kaufman, K. K. Bardhan, and R. B. Griffiths, Phys. Rev. Lett. **44**, 77 (1980).