*J. Chem. Eng. Data* **1993**, *38*, 417-421 **417**

# Three-Phase Equilibria in the Binary System Ethylene + Eicosane and the Ternary System Propane + Ethylene + Eicosane

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The solid eicosane–liquid–vapor (SLV) phase behavior in the binary system ethylene + eicosane was investigated. It was found that the SLV curve ends at a critical end point where liquid and vapor are critical in the presence of pure solid eicosane. In this binary system liquid–liquid–vapor (LLV) equilibria are metastable with respect to solid formation. Addition of propane to mixtures of ethylene and eicosane revealed stable LLV equilibria. *P–T* sections for seven ternary mixtures with different propane and eicosane concentrations were determined according to the synthetic method. On the basis of the results obtained, a rough estimate of the ternary tricritical point and the metastable binary LLV curve is performed.

## Introduction

Binary three-phase solid–liquid–vapor (SLV) curves with a critical end point where liquid and vapor are critical in the presence of a solid phase (S + L = V) can be found in two different cases (*1*, *2*). In the first case a part of the critical curve in a type I phase diagram is obscured by the formation of a solid phase. See Figure 1. The three-phase line $S_BLV$ is divided in two parts, both ending in a critical end point (p and q). In the temperature interval between the two critical end points both SLV equilibria and L = V critical points are metastable with respect to solid–fluid equilibria. The low-temperature branch of the curve usually lies very close to the vapor pressure curve, LV(A), of the light component. In the second case liquid–liquid–vapor (LLV) equilibria in a type V phase diagram are obscured by formation of the solid phase. See Figure 2. The solid–liquid–vapor curve is again divided in two branches: $S_BL1V$ and $S_BL2V$, both ending in a critical end point (p and q, respectively). Also in this case the low-temperature branch of the SLV curve lies very close to the vapor pressure curve of the light component. Now the type V L2L1V equilibrium is metastable with respect to solid–vapor equilibria. There are some possibilities to reveal this metastable equilibrium. If the distance between the melting point of pure component B, SL(B), and p is relatively small, it can be possible to subcool the system. The other possibility is to add to the system a third component which is miscible with both binary constituents. This will move the three-phase region L2L1V to higher temperatures (*3*). The shift depends mainly on the concentration of the added third component, and when this concentration is high enough, the LLV region moves out of the solid area.

Diepen and Zeeuw (*4*) reviewed the phase behavior of binary ethylene + *n*-alkane systems. Mixtures of ethylene with normal hydrocarbons from ethane to decane exhibit type I phase behavior according to the classification of van Konynenburg and Scott (*5*). The system with hexadecane shows a stable liquid–liquid–vapor phase split. Systems with octacosane and hexatriacontane show only SLV equilibria with critical end points p and q (S + L = V). According to de Loos (*6*), these systems are probably of the same type as those of Figure 2b.

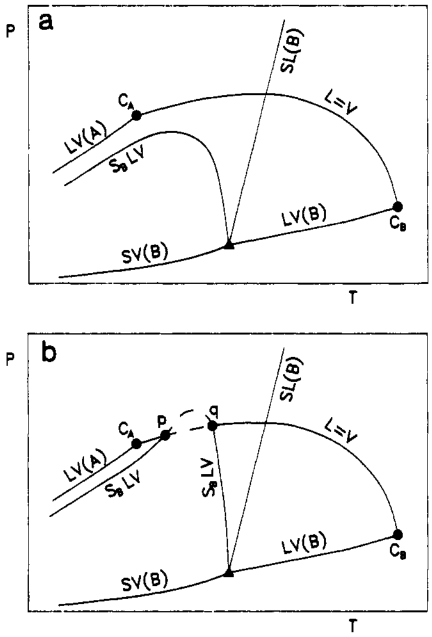

**Figure 1.** *P–T* projections of monovariant equilibria of a binary system of light (A) and heavy components (B) showing type I phase behavior: (a) continuous vapor–liquid critical curve (L = V); (b) L = V curve intersects twice with the solid–liquid–vapor curve; p, $S_B$ + L = V; q, $S_B$ + L = V.

There is no information in the literature on the system ethylene + eicosane. In this work the solid eicosane–liquid–vapor curve was measured up to a critical end point, S + L = V. This proves that the LLV phase split, if it occurs at all, is obscured entirely by the solid formation in this system. Measurements were also performed for the ternary system propane + [ethylene + eicosane] for different concentrations of eicosane on a propane-free basis ($x°_{C20}$) and for seven mole fractions of propane. In all ternary mixtures a stable LLV region is found. Rough estimates of the binary metastable LLV curve and the ternary tricritical point were also obtained on the basis of the experimental results.

## Experimental Section

The experiments were performed using a so-called Cailletet apparatus. A mixture of known composition is contained in

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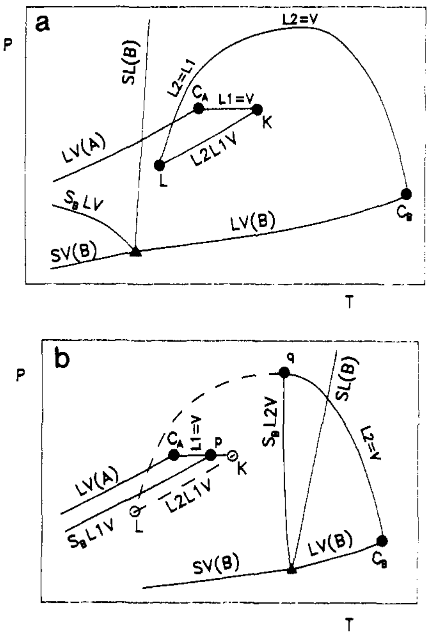

**Figure 2.** $P$–$T$ projections of monovariant equilibria of a binary system of light (A) and heavy components (B) showing stable (a) and metastable (b) type V phase behavior: K, L2 + L1 = V; L, L2 = L1 + V; p, $S_B$ + L1 = V; q, $S_B$ + L2 = V.

a glass measuring cell. Different experimental procedures were applied to measure SLV equilibria in the binary system and LLV equilibria in the ternary system. In the first case at fixed temperature the volume was changed to form the solid phase and equal volumes of liquid and vapor. Then the system was allowed to reach equilibrium. From Gibbs' phase rule one can conclude that a two-component system with three phases has 1 degree of freedom. Thus, at constant temperature our binary system had only one pressure where three phases can coexist, and this pressure was measured. Phase equilibria in the ternary mixtures were measured in a different way. At a fixed temperature the pressure where a new phase appears or an existing phase disappears can be determined visually. Boundary curves between regions of one and two phases and between regions of two and three phases can be determined in this way.

In the binary SLV measurements the pressure was measured using a Druck pressure indicator. The apparatus was calibrated with a dead weight pressure gauge. The pressure in the ternary experiments was measured directly using a dead weight pressure gauge. In both cases the accuracy of the pressure measurement was within 0.003 MPa. A platinum resistance thermometer with an accuracy of 0.01 K was used to measure the temperature. During the experiments the temperature in the water thermostat was maintained constant within 0.03 K. A more detailed description of the apparatus and the experimental procedure can be found elsewhere (*7*).

## Materials

The eicosane used in this work was obtained from Shell Research in Houston. A minimum purity of 98.0 mol % was ascertained by the producer. According to a GC analysis, its purity is 99.7 mol %, and according to a DSC analysis, its purity is 99.8 mol %. The impurities are probably homologues and will probably have a negligible effect on the phase behavior of the systems investigated.

Propane was delivered by Air Products with a minimum purity of 99.95%. To check the purity, the vapor pressure curve was measured. The mean deviation in vapor pressure between our experiments and recommended literature values (*8*) in the temperature range 303–363 K was 0.005 MPa.

**Table I. $P$–$T$ Projection of Solid Eicosane–Liquid–Vapor Equilibria in the System Ethylene + Eicosane**

| $T$/K | $P$/MPa | $T$/K | $P$/MPa | $T$/K | $P$/MPa |
|---|---|---|---|---|---|
| 243.58 | 1.952 | 277.28 | 4.475 | 283.26 | 5.106 |
| 248.34 | 2.226 | 278.20 | 4.563 | 283.30 | 5.111 |
| 253.31 | 2.534 | 278.65 | 4.615 | 283.36 | 5.116 |
| 258.36 | 2.878 | 279.23 | 4.677 | 283.41 | 5.124 |
| 263.33 | 3.247 | 279.71 | 4.724 | 283.45 | 5.128 |
| 268.47 | 3.663 | 280.29 | 4.786 | 283.49 | 5.132 |
| 273.32 | 4.094 | 280.71 | 4.829 | 283.60 | 5.145 |
| 274.13 | 4.170 | 281.30 | 4.896 | 283.65 | 5.147 |
| 274.68 | 4.240 | 281.68 | 4.937 | 283.72 | 5.153 |
| 275.74 | 4.324 | 282.22 | 4.996 | 283.76 | 5.156 |
| 276.28 | 4.376 | 282.72 | 5.054 | 283.81 | 5.162 |
| 276.78 | 4.426 | 283.21 | 5.098 | 283.84 | 5.167 p[a] |

[a] p = critical end point, S + L1 = V.

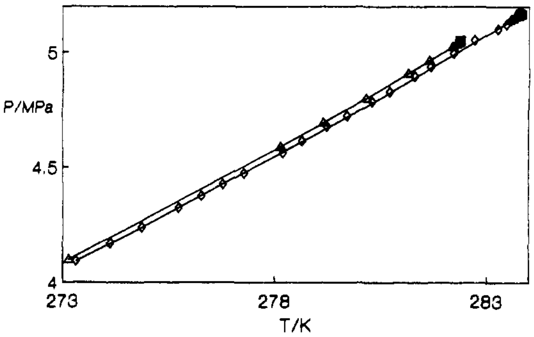

**Figure 3.** $P$–$T$ projection of solid eicosane–liquid–vapor equilibria for the binary system ethylene + eicosane. (△) L + V, C2H4 (ref 9); (◇) binary SLV; (■) L = V, C2H4 (ref 9); (●) binary S + L = V.

Ethylene was delivered by Air Products with a minimum purity of 99.95 mol %. To check the purity, the vapor pressure was measured at several temperatures. The mean deviation in vapor pressure between our experiments and the literature (*9*) was 0.005 MPa.

The eicosane, ethylene, and propane were used without further purification.

## SLV Equilibria in the System Ethylene + Eicosane

Experimental results of solid eicosane–liquid–vapor equilibrium measurements are given in Table I. Part of the data, close to the critical end point, are plotted in Figure 3 together with the vapor pressure curve of pure ethylene. Both curves lie close to each other, and at very low temperatures they practically coincide. In the binary system no LLV phase split has been observed. From results for binary systems of ethylene with other $n$-alkanes it may be concluded that in the system ethylene + eicosane the LLV curve is metastable, obscured by the occurrence of solid eicosane. The critical end point, p in Table I, is found at a temperature which is about 1.5 K higher than the critical point of ethylene.

The high-temperature branch of the solid–liquid–vapor curve was not measured.

## LLV Equilibria in the System Propane + [Ethylene + Eicosane]

To binary mixtures of ethylene + eicosane with different concentrations of the heavy component ($x^\circ_{C20}$) was added propane. Propane is fully miscible with both ethylene (*4*) and eicosane (*10*). According to Luks (*3*), the three-phase LLV region will be shifted to higher temperatures with

**Table II. Fluid-Phase Equilibria in the System Ethylene + Propane + Eicosane: Boundaries of Three-Phase and Two-Phase Regions for a Given Composition**

| | P/MPa | | | | P/MPa | | | | P/MPa | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| T/K | L2/L1 + V → L2 + L1 + V | L2 + L1 + V → L1 + L2/V | L1 + L2/V → L2/L1 | T/K | L2/L1 + V → L2 + L1 + V | L2 + L1 + V → L1 + L2/V | L1 + L2/V → L2/L1 | T/K | L2/L1 + V → L2 + L1 + V | L2 + L1 + V → L1 + L2/V | L1 + L2/V → L2/L1 |
| $x_{C3} = 0.0566$, $x^{\circ}_{C20} = 0.0072$ | | | | | | | | | | | |
| 290.46 | 5.181 | 5.365 | 6.059 | 290.59 | 5.201 | 5.375 | 6.089 | 291.11 | 5.281 | 5.400 | 6.209 |
| 290.47 | 5.176 | 5.365 | 6.064 | 290.85 | 5.241 | 5.390 | 6.149 | 291.17 | 5.291 | 5.405[a] | 6.214 |
| 290.48 | 5.181 | 5.365 | 6.069 | 290.91 | 5.251 | 5.395 | 6.174 | | | | |
| $x_{C3} = 0.0822$, $x^{\circ}_{C20} = 0.0070$ | | | | | | | | | | | |
| 289.92 | 4.774 | 5.116 | 5.281 | 291.17 | | 5.241 | 5.521 | 294.41 | 5.293 | 5.506 | 6.126 |
| 290.18 | 4.784 | 5.146 | 5.326 | 291.77 | 4.928 | 5.301 | 5.641 | 294.47 | 5.298 | 5.511 | 6.131 |
| 290.44 | 4.804[b] | 5.176 | 5.386 | 292.30 | 4.983 | 5.346 | 5.746 | 294.48 | 5.303 | 5.511 | 6.141 |
| 290.50 | 4.804 | 5.176 | 5.391 | 292.78 | 5.043 | 5.391 | 5.831 | 294.53 | 5.308 | 5.511[a] | 6.146 |
| 290.53 | 4.804 | 5.181 | 5.396 | 293.27 | 5.108 | 5.431 | 5.926 | 294.59 | 5.318 | 5.511 | 6.161 |
| 290.60 | 4.809 | 5.186 | 5.411 | 293.74 | 5.178 | 5.471 | 6.016 | 294.81 | 5.353 | 5.516 | 6.206 |
| 291.08 | 4.853 | 5.231 | 5.506 | 294.24 | 5.258 | 5.496 | 6.106 | | | | |
| $x_{C3} = 0.0944$, $x^{\circ}_{C20} = 0.0095$ | | | | | | | | | | | |
| 290.11 | 4.798 | 5.116 | 5.421 | 292.76 | 4.988 | 5.366 | 5.951 | 295.24 | 5.332 | 5.546 | 6.436 |
| 290.48 | 4.813 | 5.151 | 5.496 | 293.24 | 5.048 | 5.406 | 6.041 | 295.29 | 5.332 | 5.546[a] | 6.441 |
| 290.75 | 4.828 | 5.172 | 5.556 | 293.72 | 5.103 | 5.446 | 6.136 | 295.61 | 5.387 | 5.551 | 6.496 |
| 290.91 | 4.838[b] | 5.191 | 5.581 | 294.33 | 5.192 | 5.496 | 6.261 | 295.88 | 5.457 | 5.551 | 6.546 |
| 291.02 | 4.843 | 5.201 | 5.611 | 294.70 | 5.243 | 5.521 | 6.321 | 295.98 | 5.492 | 5.546 | 6.561 |
| 291.33 | 4.863 | 5.231 | 5.671 | 295.17 | 5.317 | 5.541 | 6.421 | 296.26 | | | 6.611 |
| 292.34 | 4.943 | 5.326 | 5.861 | 295.20 | 5.322 | 5.541 | 6.421 | | | | |
| $x_{C3} = 0.1120$, $x^{\circ}_{C20} = 0.0542$ | | | | | | | | | | | |
| 289.72 | 4.873 | 4.993 | 5.703 | 291.16 | 4.998 | 5.133 | 6.013 | 295.13 | 5.397 | 5.517 | 6.847 |
| 289.74 | 4.872 | 4.997 | 5.702 | 291.24 | 5.002 | 5.142 | 6.027 | 296.19 | 5.532 | 5.592[a] | 7.067 |
| 289.75 | 4.873 | 4.998 | 5.708 | 292.14 | 5.082 | 5.227 | 6.217 | 296.44 | 5.582 | 5.582 | |
| 290.17 | 4.908 | 5.038 | 5.798 | 293.14 | 5.182 | 5.327 | 6.432 | 297.18 | | | 7.267 |
| 290.20 | 4.913 | 5.043 | 5.803 | 294.15 | 5.292 | 5.422 | 6.642 | | | | |
| $x_{C3} = 0.1508$, $x^{\circ}_{C20} = 0.0423$ | | | | | | | | | | | |
| 288.73 | | | 4.631 | 292.17 | 4.897 | 4.957 | 5.182 | 298.14 | 5.372 | 5.517 | 6.427 |
| 289.21 | | | 4.676 | 293.17 | 4.967 | 5.047 | 5.397 | 299.09 | 5.467 | 5.602 | 6.622 |
| 290.15 | | | 4.766 | 294.14 | 5.037 | 5.142 | 5.602 | 300.15 | 5.582 | 5.682 | 6.837 |
| 290.36 | | | 4.791 | 295.15 | 5.112 | 5.237 | 5.812 | 300.44 | 5.627 | 5.692 | |
| 290.62 | 4.801 | 4.811 | 4.851 | 296.11 | 5.187 | 5.327 | 6.012 | 300.63 | 5.657 | 5.697 | 6.932 |
| 291.16 | 4.837 | 4.862 | 4.962 | 297.12 | 5.277 | 5.422 | 6.222 | | | | |
| $x_{C3} = 0.1527$, $x^{\circ}_{C20} = 0.0245$ | | | | | | | | | | | |
| 292.76 | | | 4.953 | 297.05 | 5.170[b] | 5.344 | 5.814 | 301.91 | | 5.729 | 6.784 |
| 293.34 | 4.984 | 5.009 | 5.059 | 297.07 | 5.175 | 5.349 | 5.824 | 301.92 | 5.565 | 5.729 | 6.784 |
| 293.50 | 4.993 | 5.018 | 5.098 | 297.28 | 5.184 | 5.369 | 5.869 | 301.95 | 5.565 | 5.729 | 6.794 |
| 293.77 | 4.998 | 5.033 | 5.123 | 297.76 | 5.209 | 5.414 | 5.964 | 301.98 | 5.560 | 5.734[a] | 6.799 |
| 294.25 | 5.028 | 5.088 | 5.253 | 298.46 | 5.249 | 5.474 | 6.104 | 301.99 | 5.570 | 5.729 | 6.799 |
| 295.26 | 5.073 | 5.183 | 5.458 | 299.58 | 5.330 | 5.574 | 6.329 | 302.01 | | 5.730 | 6.804 |
| 295.74 | 5.103 | 5.228 | 5.558 | 301.27 | 5.484 | 5.729 | 6.664 | 302.38 | 5.644 | 5.739 | |
| 296.22 | 5.123 | 5.273 | 5.653 | 301.80 | 5.545 | 5.724 | 6.764 | | | | |
| 296.76 | 5.154 | 5.319 | 5.764 | 301.89 | 5.555 | 5.724 | 6.774 | | | | |
| $x_{C3} = 0.1982$, $x^{\circ}_{C20} = 0.0049$ | | | | | | | | | | | |
| 307.19 | | | 5.852 | 308.25 | 5.827 | 5.906 | 5.996 | 309.40 | 5.807 | 5.932 | 6.161 |
| 307.46 | 5.867 | 5.872 | 5.877 | 308.62 | 5.822 | 5.916 | 6.051 | 309.88 | 5.807 | 5.932 | 6.229 |
| 307.56 | 5.872 | 5.877 | 5.897 | 308.70 | 5.822 | 5.916[a] | 6.061 | 310.25 | 5.822 | 5.917 | 6.281 |
| 307.72 | 5.862 | 5.882 | 5.917 | 308.78 | 5.817 | 5.921 | 6.071 | 310.33 | 5.829[b] | 5.916 | 6.291 |
| 307.83 | 5.857 | 5.887 | 5.932 | 308.82 | 5.817 | 5.922 | 6.081 | 310.41 | 5.832 | 5.906 | 5.306 |
| 307.96 | 5.847 | 5.896 | 5.956 | 309.03 | 5.812 | 5.927 | 6.106 | | | | |

[a] L2 + L1 = V. [b] L2 = L1 + V.

increasing propane concentration, and we believe that this effect is independent whether the binary LLV curve is stable or metastable.

Seven ternary mixtures, C3 + [C2H4 + C20], with the compositions $x_{C3} = 0.0566$, $x^{\circ}_{C20} = 0.0072$; $x_{C3} = 0.0822$, $x^{\circ}_{C20} = 0.0070$; $x_{C3} = 0.0944$, $x^{\circ}_{C20} = 0.0095$; $x_{C3} = 0.1120$, $x^{\circ}_{C20} = 0.0542$; $x_{C3} = 0.1508$, $x^{\circ}_{C20} = 0.0423$; $x_{C3} = 0.1527$, $x^{\circ}_{C20} = 0.0245$; and $x_{C3} = 0.1982$, $x^{\circ}_{C20} = 0.0492$ were investigated. All results are given in Table II and plotted in Figure 4. In all ternary mixtures investigated a stable L2L1V region was found. Qualitatively the same type of behavior was found as in the system propane + [ethane + eicosane] (*11*).

The existence of a stable LLV region depends on the concentrations of propane and eicosane. A concentration of propane of less than 5 mol % is not enough to move the metastable LLV region out of the solid–fluid area. The Q-point curve where four phases (solid–liquid–liquid–vapor) coexist is the border line between the stable and metastable part of the three-phase L2L1V region for the ternary system. This curve is usually steep in the *P*–*T* projection and extends from the K- to the L-point curve. See Figure 5. The Q-point curve was not measured precisely, but its position can be established from Figure 4a,d at 290 K.

It was observed for the system C3 + C2 + C20 that a line drawn from the K point to the L point for a given mixture is approximately parallel to the L2L1V curve (*11*). For the system investigated here this is not the case. The L-point temperature can even be higher than the K-point temperature

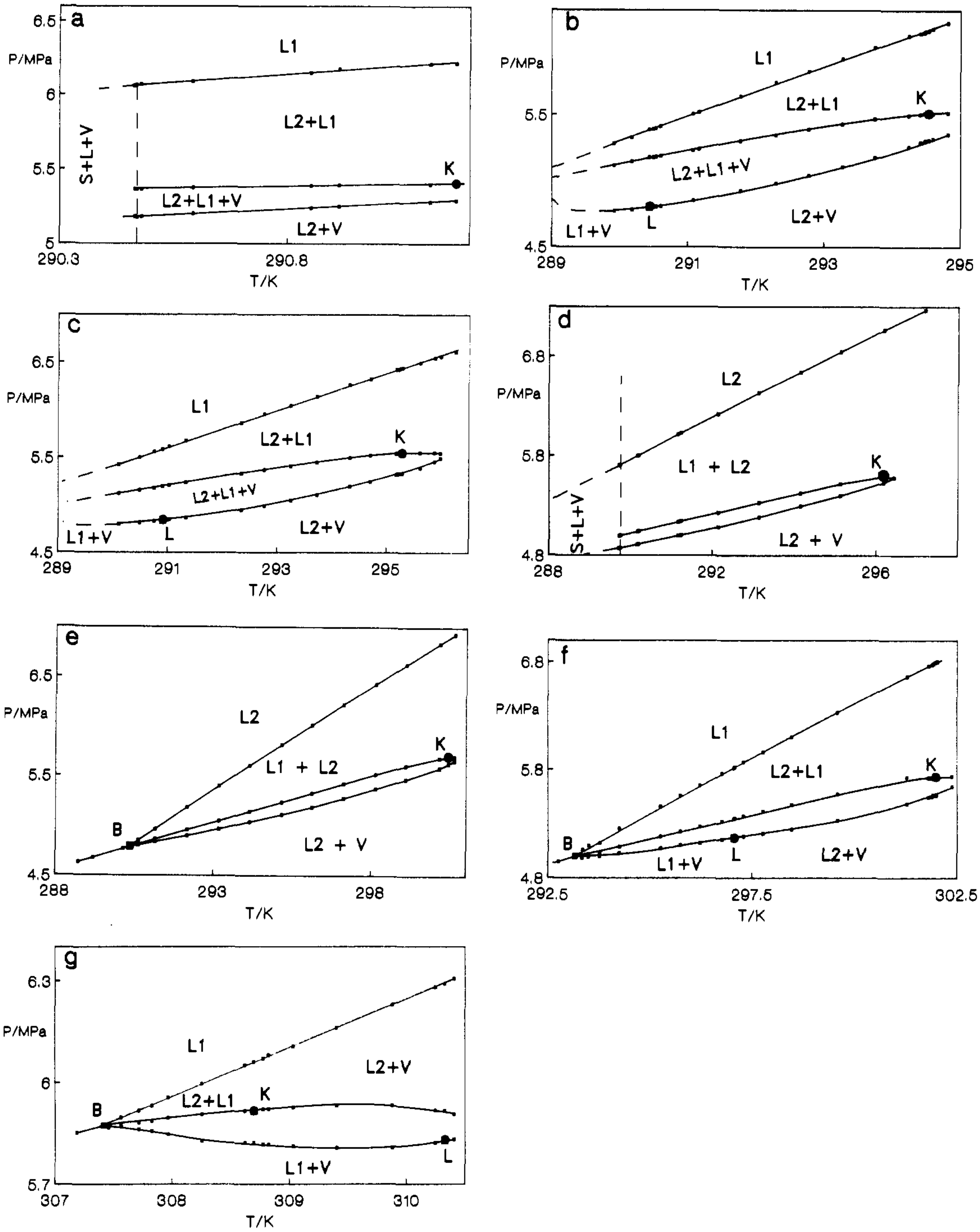

**Figure 4.** Fluid-phase equilibria in the system $\{x_{C3}$ C3H8 + $(1 - x_{C3})$ $[(1 - x^{\circ}_{C20})$ C2H4 + $x^{\circ}_{C20}$ C20H42$]\}$, *P–T* sections for constant overall composition: (a) $x_{C3} = 0.0566$, $x^{\circ}_{C20} = 0.0072$; (b) $x_{C3} = 0.0822$, $x^{\circ}_{C20} = 0.0070$; (c) $x_{C3} = 0.0944$, $x^{\circ}_{C20} = 0.0095$; (d) $x_{C3} = 0.1120$, $x^{\circ}_{C20} = 0.0542$; (e) $x_{C3} = 0.1508$, $x^{\circ}_{C20} = 0.0423$; (f) $x_{C3} = 0.1527$, $x^{\circ}_{C20} = 0.0245$; (g) $x_{C3} = 0.1982$, $x^{\circ}_{C20} = 0.0492$; K, L2 + L1 = V; L, L2 = L1 + V.

as shown in Figure 4g for a mixture of $x_{C3} = 0.1982$ and $x^{\circ}_{C20} = 0.0492$.

On the basis of ternary K- and L-point measurements, metastable critical end points for the binary ethylene + eicosane mixture were estimated. To do this, the following assumptions were made: The K- and L-point curves of the ternary system can be approximated by straight lines in the whole temperature interval. The critical end point of ethylene, the critical end point S + L1 = V, and the metastable K point lie on the same straight line. The metastable L2L1V curve is parallel to the SL1V curve. For the binary K and L points the following coordinates were found: (284.6 K, 5.23 MPa) and (270.0 K, 3.75 MPa). See also Figure 5.

A rough estimate of the coordinates of the tricritical point was found as an intersection of ternary K- and L-point curves. The following values were found: 316.4 K and 6.15 MPa.

## Conclusions

The binary system ethylene + eicosane shows SL1V phase equilibria with a critical end point S + L1 = V and a metastable L2L1V curve.

Addition of propane to this binary system revealed a stable liquid–liquid–vapor phase split. In general one can say that the differentiation between the phase behavior as shown in

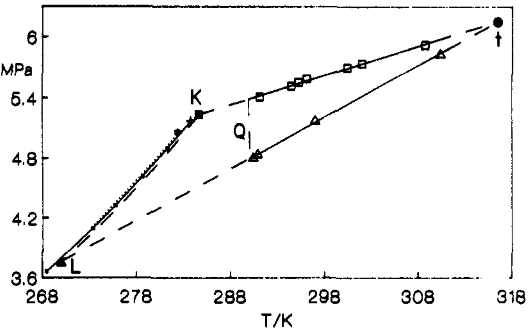

**Figure 5.** L2L1V equilibria in the system ethylene + propane + eicosane, *P–T* projection of K- and L-point curves: K, L2 + L1 = V; L, L2 = L1 + V; Q, S + L2 + L1 + V; t, L2 = L1 = V; ∗, L = V for C2H4; +, $S_B$ + L1 = V for C2H4 + C20H42; (···) C2H4 vapor pressure curve; (■) $S_B$ + L1 + V for C2H4 + C20H42.

Figures 1b and 2b can only be made on the basis of ternary experiments.

## Acknowledgment

The authors acknowledge technical assistance by Mr. Saban Yildirim.

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Received for review October 8, 1992. Accepted February 18, 1993. J.G. acknowledges the Delft University of Technology for financial support.