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Liquid–Liquid–Vapor Equilibria in Binary Families of SF_6, $CClF_3$, $C_2H_3F_3$, and C_2H_4 with *n*-Alkanes[1]

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Liquid–liquid–vapor equilibria were determined experimentally for binary and quasi-binary systems which consisted of a low-volatile *n*-alkane or mixture of *n*-alkanes with a more volatile component, chlorotrifluoromethane, sulfur hexafluoride, 1,1,1-trifluoroethane, and ethene. From the location of the critical endpoints $L_2 = L_1 + V$ and $L_2 + L_1 = V$ of the three-phase curves, the coordinates of the tricritical point and the double critical endpoint of these families were estimated by extrapolation. For the families studied it was found that increasing the carbon number of the *n*-alkane leads to a transition from type II to type IV to type III fluid phase behavior.

KEY WORDS: chlorotrifluoromethane; dodecane; double critical endpoint; ethene; heptadecane; hexadecane; liquid–liquid–vapor equilibria; nonane; octadecane; octane; pentadecane; sulfur hexafluoride; tetradecane; tricritical point; tridecane; 1,1,1-trifluoroethane; undecane.

1. INTRODUCTION

Binary mixtures, consisting of a more volatile component such as carbon dioxide, ethane, or nitrous oxide and a low-volatile component such as a long-chain *n*-alkane, may exhibit liquid–liquid immiscibility phenomena extended at low- and/or at high (near the critical point of the more volatile component)-temperature regions [1, 2]. These systems can be classified according to the classification scheme of van Konynenburg and Scott [3] as type II, III, IV, or V. A family of binary mixtures where the less-volatile

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component is changing systematically as a member of the same homologous series, such as the *n*-alkanes, and even continuously by appropriate mixing of two successive members of the same homologous series (quasi-binary mixtures), offers the possibility of a methodical study of the transitions between these types of fluid phase behavior.

In Fig. 1 the transition from type II to type IV is illustrated. Type II shows, in the *P*, *T*-projection, a low-temperature region of liquid–liquid equilibria, which is restricted to high temperatures by a liquid–liquid critical curve (——△) and at low pressures by a three-phase liquid–liquid–

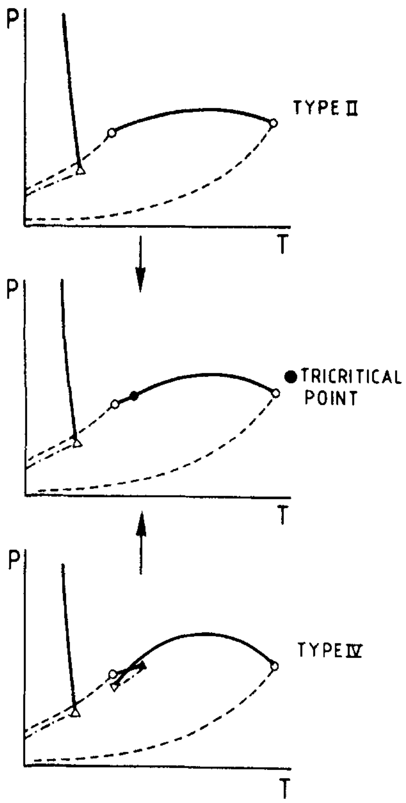

Fig. 1. Transition from type II to type IV fluid phase behavior. (-----) Vapor pressure curves; (—·—·-) liquid–liquid–vapor curve; (——) critical curves. (○) Critical point; (△) UCEP $L_2 = L_1 + V$; (▽) LCEP $L_2 = L_1 + V$; (▲) UCEP $L_2 + L_1 = V$; (●) tricritical point.

vapor curve (—-—-△). These two curves intersect in the upper critical *endpoint (UCEP; △) $L_2 = L_1 + V$ of the three-phase curve. At this point* a critical liquid phase $L_2 = L_1$ is in equilibrium with a noncritical vapor phase V. The vapor–liquid critical line (○——○) is a continuous curve between the critical points of the two pure components. In type IV the same low-temperature region of liquid–liquid equilibria is found, but this type shows, at high temperatures, a second region of liquid–liquid immiscibility which is bounded at low pressures by a second branch of the three-phase liquid–liquid–vapor curve (▽—-—-▲). The vapor–liquid critical curve is broken into two parts. The first part ($L_1 = V$; ○——▲) starts at the critical point of the more volatile component and intersects the high-temperature branch of the three-phase curve in an UCEP $L_2 + L_1 = V$. At this point a critical phase $L_1 = V$ is in equilibrium with the noncritical liquid phase L_2. The second part (○——▽) starts at the critical point of the low-volatile component and intersects the high-temperature branch of the three-phase curve in a lower critical endpoint (LCEP) $L_2 = L_1 + V$. At low temperatures this branch of the critical curve is a liquid–liquid critical curve, but it changes at high temperatures gradually into a vapor–liquid critical curve. The transition between these two types of fluid phase behavior occurs via a so-called tricritical point (TCP), $L_2 = L_1 = V$ (●), where the LCEP and the UCEP of the high-temperature branch of the three-phase curve coincide and the three-phase curve has a zero length. Transitions between type V and type I fluid phase behavior are similar. In these types the low-temperature region of liquid–liquid equilibria is missing.

The transition between type IV and type III fluid phase behavior is illustrated in Fig. 2. In type III the low-temperature branch and the high-temperature branch of the liquid–liquid–vapor curve are merged into one three-phase curve (—-—-▲), and also, the two liquid–liquid critical curves found in type IV are joined. The transition occurs via a so-called double critical endpoint (DCEP) (●), where the UCEP of the low-temperature branch of the three-phase curve coincides with the LCEP of the high-temperature branch of this curve. The liquid–liquid critical curve is tangent to the three-phase curve in the DCEP.

In the binary families of nitrous oxide [4], ammonia [5], and perfluoromethane [6, 7] with members of the homologous series of the *n*-alkanes, transitions from type II to type III phase behavior are found with increasing carbon number of the *n*-alkane. According to the calculations of van Konynenburg and Scott, these transitions occur via the intermediate type IV, as has actually been found in the family of carbon dioxide +*n*-alkanes [8, 9]. For a binary system the number of degrees of freedom according to the phase rule is negative at a TCP or a DCEP. This implies

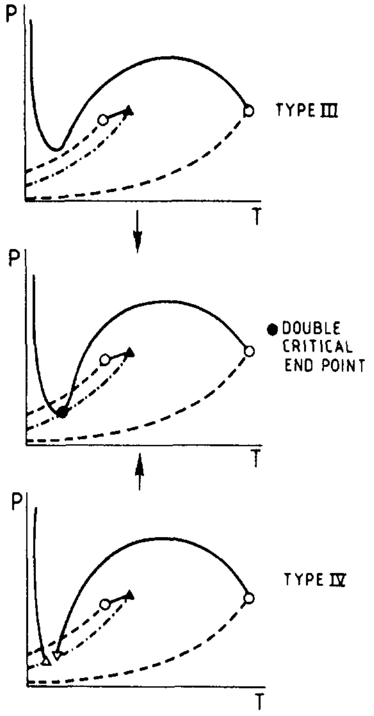

Fig. 2. Transition from type IV to type III fluid phase behavior. (spadesuit) Vapor pressure curves; (— - —-) liquid–liquid–vapor curve; (———) critical curves. (○) Critical point; (△) UCEP $L_2 = L_1 + V$; (▽) LCEP $L_2 = L_1 + V$; (▲) UCEP $L_2 + L_1 = V$; (●) double critical point.

that it is very unlikely to find a TCP or a DCEP in a binary system. Creek et al. [10] and Goh et al. [11] have shown that the TCP can be approached very closely by studying quasi-binary systems: systems of the light component and a pseudo-component prepared by mixing of two nearest neighbors of the *n*-alkane series.

Investigations of this kind are important in the chemical industry, e.g., in supercritical fluid technology, where the most commonly used supercritical solvent is carbon dioxide. In this paper experimental results are presented for the families of ethene (C_2H_4), chlorotrifluoromethane ($CClF_3$), 1,1,1-trifluoroethane ($C_2H_3F_3$), and sulfur hexafluoride (SF_6) with *n*-alkanes.

2. MEASUREMENTS

2.1. Specimens

Details concerning the supplier and the purity of the chemicals used are given in Table I. To check the purity of the gases, we measured their vapor pressures. Our results agreed with literature data [12–15] within the experimental uncertainty.

2.2. Procedure

The measurements were carried out in a glass-tube apparatus at pressures up to 15 MPa and temperatures up to 530 K, as described earlier by de Loos et al. [16]. With this so-called Cailletet apparatus, phase envelopes of mixtures of known composition and monovariant multiphase equilibria could be visually determined. A sample of the mixture with known composition was present in a narrow glass tube, mounted in a thermostat with circulating water or a circulating (water + alcohol) mixture, which maintained a constant temperature within 0.02 K. Mercury was used as a pressure intermediate between the sample and the oil in the pressure generating system. The temperature was measured with a 100-Ω platinum resistance thermometer (ASL F-16), calibrated against a standard thermometer. The uncertainty in the measured temperature was approximately 0.02 K. The pressure was measured with a deadweight gauge (de Wit) with an uncertainty of approximately 2 kPa.

Table I. Chemicals Used in the Present Study

Compound	Supplier	Purity (%)
Ethene	Aga	99.95
Chlorotrifluoromethane	Praxair	99
1,1,1-Trifluoroethane	Intermar	99
Sulfur hexafluoride	Air Products	99.8
Octane	Fluka	99.8
Nonane	Fluka	99.5
Undecane	Fluka	99.5
Dodecane	Merck	99.5
Tridecane	Fluka	99.5
Tetradecane	Fluka	99.5
Pentadecane	Fluka	99.8
Hexadecane	Merck	99.5
Heptadecane	Janssen Chimica	99
Octadecane	Fluka	99

The mixtures are prepared by dosing the low-volatile liquid component or the mixture of two low-volatile liquid components in the sealed end of the Cailletet tube by means of a micrometer syringe. The exact mass of the liquid is determined by weighing. The liquid is thoroughly degassed by successive freezing and melting under high vacuum. To guarantee that no low-volatile components are lost, the sample is cooled with liquid nitrogen during each evacuation step. The gaseous component is added volumetrically using a mercury displacement method [17].

For the measurement of the liquid–liquid–vapor equilibrium pressures, the volume of the sample is adjusted until the three-phase equilibrium state is observed visually. In the case of experiments on quasi-binary systems, no variation of the three-phase equilibrium pressure could be observed within the experimental uncertainty when the volume was varied in the interval in which the three-phase equilibrium is stable. At a $L_2 + L_1 = V$ critical endpoint, the three-phase curve ends in a point in which the top phase and the middle phase are critical, and at a $L_2 = L_1 + V$ critical endpoint, the liquid–liquid–vapor curve ends in a point where the bottom phase and the middle phase are critical. The uncertainty in the experimental critical endpoint temperature is 0.02 K.

3. RESULTS AND DISCUSSION

In Fig. 3, the liquid–liquid–vapor three-phase pressure of the binary systems SF_6 + octane and SF_6 + nonane is presented as a function of temperature. The three-phase curve of SF_6 + octane ends in an UCEP $L_2 = L_1 + V$, so this binary system is a type II system. The three-phase curve of SF_6 + nonane ends in an UCEP $L_2 + L_1 = V$ and goes uninterrupted to low temperatures. So this binary system is a type III system. To study the transition from type II to type III, the phase behavior of quasi-binary systems of SF_6 and pseudo-components composed of a mixture of octane and nonane was studied. The experimental three-phase curve for SF_6 and a mixture of octane and nonane with an average carbon number n of 8.5379 is also plotted in Fig. 3. This curve shows a low-temperature branch ending in an UCEP $L_2 = L_1 + V$ and a high-temperature branch starting in a LCEP $L_2 = L_1 + V$ and ending in an UCEP $L_2 + L_1 = V$. So this quasi-binary system is a type IV system. The coordinates of the critical endpoints of this and other quasi-binary mixtures are presented in Table II and plotted in Fig. 4. Although the quasi-binary systems are in fact ternary systems and, for this reason, these systems should show a three-phase region instead of a three-phase curve, it was found experimentally that the width of the three-phase region could not be measured within the

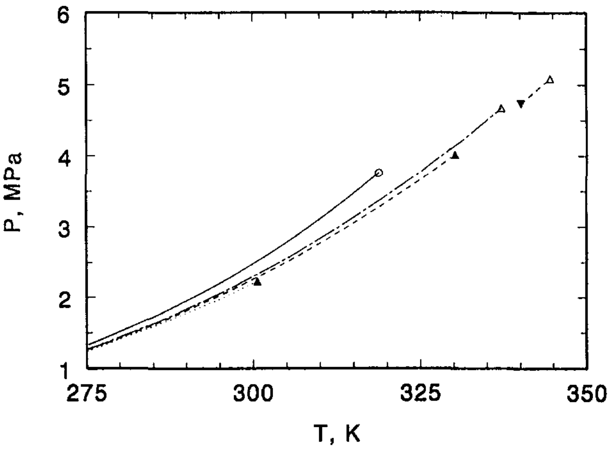

Fig. 3. Monovariant equilibria in the $SF_6 + n$-alkane family (——) Vapor pressure curve of SF_6; (— - —) liquid–liquid–vapor curve SF_6 + nonane; (-----) liquid–liquid–vapor curve $SF_6 + C_{8.5379}$; (···) liquid–liquid–vapor curve SF_6 + octane. (○) Critical point; (▲) UCEP $L_2 = L_1 + V$; (▼) LCEP $L_2 = L_1 + V$; (△) UCEP $L_2 + L_1 = V$.

Table II. Temperature and Pressure of the Critical Endpoints in the $SF_6 + n$-Alkane Family at a Given Average Carbon Number n of the n-Alkane

	UCEP $L_2 = L_1 + V$		LCEP $L_2 = L_1 + V$		UCEP $L_2 + L_1 = V$	
n	T (K)	P (MPa)	T (K)	P (MPa)	T (K)	P (MPa)
8	300.67	2.230				
8.4573	322.28	3.460	346.37	5.180	346.60	5.200
8.4653	322.85	3.450	345.94	5.110	346.50	5.140
8.4792	323.92	3.575	345.19	5.115	346.05	5.180
8.4896	324.85	3.640	344.68	5.070	345.83	5.160
8.5103	326.57	3.760	343.30	4.960	345.35	5.125
8.5249	328.27	3.890	341.54	4.840	344.85	5.100
8.5379	330.21	4.015	340.17	4.740	344.61	5.090
8.5437	332.36	4.150	338.10	4.470	344.39	5.060
8.5485					344.27	5.065
8.7504					340.37	4.850
9					337.23	4.675

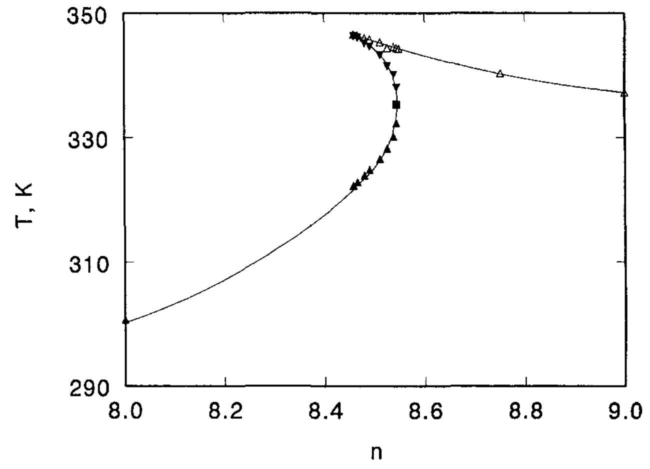

Fig. 4. The family of $SF_6 + n$-alkanes: critical endpoint temperature as a function of the average carbon number n of the n-alkane. (▲) UCEP $L_2 = L_1 + V$; (▼) LCEP $L_2 = L_1 + V$; (△) UCEP $L_2 = L_1 + V$; (●) tricritical point; (■) double critical endpoint.

experimental uncertainty. This proves that the quasi-binary systems can be treated as binary systems.

Figure 4 shows the transition from type II to type III via type IV phase behavior. The same pattern was found for the family of carbon dioxide + n-alkanes, although, in this family, type IV fluid phase behavior is found in a real binary system: carbon dioxide + tridecane [8, 9]. At low carbon numbers between 8 and 8.44, only an UCEP $L_2 = L_1 + V$ is found (type II phase behavior). At carbon numbers between 8.44 and 8.55 an UCEP $L_2 = L_1 + V$, a LCEP $L_2 = L_1 + V$, and an UCEP $L_2 + L_1 = V$ are found (type IV phase behavior), and at higher carbon numbers, only an UCEP $L_2 + L_1 = V$ is found (type III phase behavior). The tricritical point is found where the LCEP $L_2 = L_1 + V$ curve meets the UCEP $L_2 + L_1 = V$ curve in a beakpoint. The double critical endpoint is found where the UCEP $L_2 = L_1 + V$ curve and the LCEP $L_2 = L_1 + V$ curve meet in a maximum in average carbon number. We have fitted the curve through the UCEP's and the LCEP's $L_2 = L_1 + V$ with a function of the form

$$(n - n_{\mathrm{DCEP}}) = k(T - T_{\mathrm{DCEP}})^2 \tag{1}$$

It was found that this function describes the data very well. From this fit the coordinates of the DCEP were found: $n_{\mathrm{DCEP}} = 8.55$ and $T_{\mathrm{DCEP}} = 335.4$ K. The coordinates of the tricritical point were determined using the

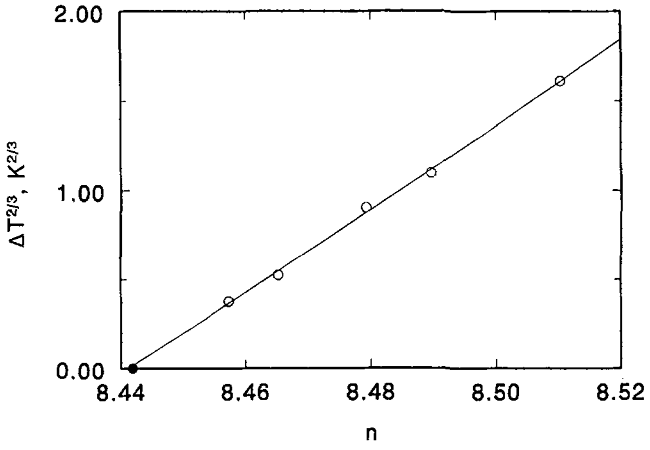

Fig. 5. The family of $SF_6 + n$-alkanes: $(\Delta T)^{2/3}$ as a function of the average carbon number n of the n-alkane.

classical theory of tricritical points of Griffiths [18] and Scott [19], using the quasi-binary approximation [10, 11]. According to this theory the following two expressions should hold close to the tricritical point:

$$T_m = (T_{\mathrm{UCEP}} + T_{\mathrm{LCEP}})/2 = T_{\mathrm{TCP}} + j_1(n - n_{\mathrm{TCP}}) \qquad (2)$$

$$\Delta T = T_{\mathrm{UCEP}} - T_{\mathrm{LCEP}}) = 2j_2(n - n_{\mathrm{TCP}})^{3/2} \qquad (3)$$

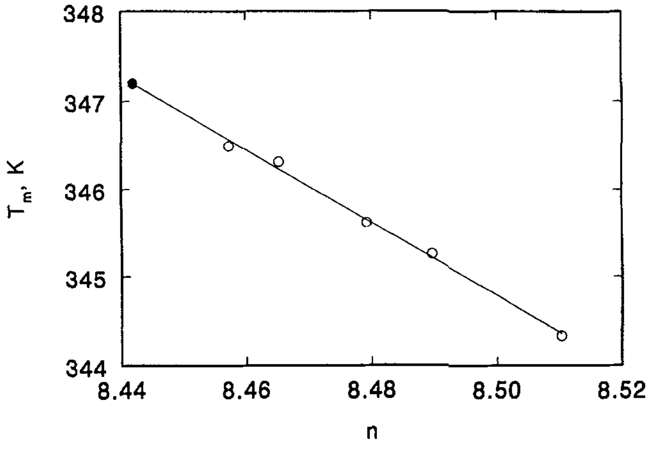

Fig. 6. The family of $SF_6 + n$-alkanes: T_m as a function of the average carbon number n of the n-alkane.

Table III. Temperature and Pressure of the Critical Endpoints in the $C_2H_3F_3 + n$-Alkane Family at a Given Average Carbon Number *n* of the *n*-Alkane

	UCEP $L_2 = L_1 + V$		LCEP $L_2 = L_1 + V$		UCEP $L_2 + L_1 = V$	
n	*T* (K)	*P* (MPa)	*T* (K)	*P* (MPa)	*T* (K)	*P* (MPa)
10	287.38	0.897				
11.	305.89	1.447				
11.6749	322.34	2.112	368.20	5.048	368.38	5.065
11.7498	324.66	2.215	366.63	4.926	367.49	5.002
11.8099	326.54	2.314	365.24	4.825	366.90	4.971
11.8999	329.68	2.477	362.62	4.621	365.90	4.905
11.9501	331.68	2.577	360.99	4.501	365.42	4.876
12.	333.77	2.692	359.23	4.363	364.99	4.842
12.040	336.25	2.836	357.05	4.200	364.61	4.820
12.082	339.42	3.023	354.18	3.998	364.25	4.801
12.101	341.25	3.131	n.a.		n.a.	
12.113	343.34	3.259	350.54	3.735	363.91	4.773
12.125					363.84	4.773
12.148					363.56	4.752
12.201					363.15	4.727
12.396					361.52	4.630
12.445					361.28	4.617
13					385.17	4.439

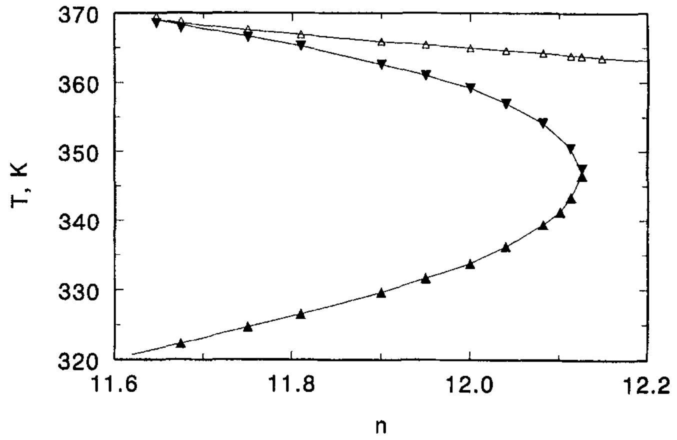

Fig. 7. The family of $C_2H_3F_3 + n$-alkanes: critical endpoint temperature as a function of the average carbon number *n* of the *n*-alkane. (▲) UCEP $L_2 = L_1 + V$; (▼) LCEP $L_2 = L_1 + V$; (△) UCEP $L_2 + L_1 = V$.

The amplitudes j_1 and j_2 are system-dependent constants. The carbon number in the tricritical point n_{TCP} is found from a plot of $(\Delta T)^{2/3}$ as a function of n by extrapolation to $(\Delta T)^{2/3}=0$, as shown in Fig. 5. The experimental points are found on a straight line as predicted by Eq. (2). The tricritical temperature T_{TCP} is found from a plot of T_m as a function of n by extrapolating to $n=n_{\mathrm{TCP}}$; see Fig. 6. Again, a straight line is found as predicted from Eq. (3). We found $n_{\mathrm{TCP}}=8.442$ and $T_{\mathrm{TCP}}=347.2$ K.

The family of $C_2H_3F_3+n$-alkanes shows the same behavior as the family of SF_6+n-alkanes. $C_2H_3F_3$ + undecane is a type II system, $C_2H_3F_3$ + dodecane is a type IV system, and $C_2H_3F_3$ + tridecane is a type III system. In Table III and Fig. 7 the coordinates of the critical endpoints of quasi-binary systems of $C_2H_3F_3$ + [undecane + dodecane] and $C_2H_3F_3$ + [dodecane + tridecane] are presented as a function of the average carbon number of the n-alkane mixture. In this family the DCEP is found at $n_{\mathrm{DCEP}}=12.13$ and $T_{\mathrm{DCEP}}=347.0$ K and the TCP at $n_{\mathrm{TCP}}=11.647$ and $T_{\mathrm{TCP}}=368.9$ K.

In Table IV the coordinates of the critical endpoints of the liquid–liquid–vapor equilibria in the $CClF_3+n$-alkane family are presented. The system $CClF_3$ + tridecane is a type III system. For the $CClF_3$ + dodecane system, only a LCEP $L_2=L_1+V$ and an UCEP $L_2+L_1=V$ are found. Based on this one would conclude that this system is a type V system. However Fig. 8, in which the critical endpoints of quasi-binary systems of $CClF_3$ + [undecane + dodecane] and of $CClF_3$ + [dodecane + tridecane] are plotted, shows the same trends as in Figs. 4 and 7. The open squares in Fig. 8 represent quadruple points of solid–liquid–liquid-vapor, in which the low-temperature branch of the liquid–liquid–vapor curve ends at low pressures. The data on which this figure are based are presented in Tables IV and V. For this family we find $n_{\mathrm{DCEP}}=12.54$ and $T_{\mathrm{DCEP}}=280.6$ K and

Table IV. Temperature and Pressure of the Critical Endpoints in the $CClF_3+n$-Alkane Family at a Given Average Carbon Number n of the n-Alkane

	UCEP $L_2=L_1+V$		LCEP $L_2=L_1+V$		UCEP $L_2+L_1=V$	
n	T (K)	P (MPa)	T (K)	P (MPa)	T (K)	P (MPa)
11.5986			315.10	4.727	316.95	4.912
11.8131			311.32	4.420	315.48	4.815
11			307.36	4.100	314.25	4.735
12.1007	255.17	1.180	304.22	3.940	313.40	4.720
12.2007	258.37	1.280	301.98	3.681	312.97	4.660
12.3751	265.56	1.567	295.46	3.222	312.23	4.597
12.4807	272.44	1.895	290.08	2.860	311.86	4.558

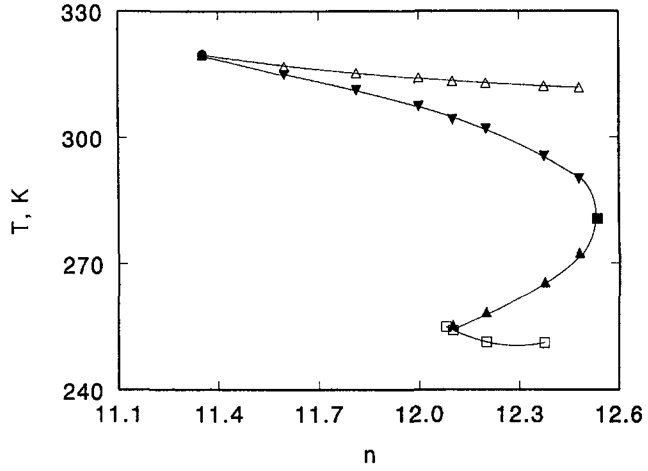

Fig. 8. The family of $CClF_3 + n$-alkanes: critical endpoint temperature as a function of the average carbon number n of the n-alkane. (▲) UCEP $L_2 = L_1 + V$; (▼) LCEP $L_2 = L_1 + V$; (△) UCEP $L_2 + L_1 = V$; (●) tricritical point; (■) double critical endpoint; (□) quadruple-point solid–liquid–liquid–vapor.

$n_{TCP} = 11.353$ and $T_{TCP} = 319.8$ K. Figure 8 clearly shows that the observation of the low-temperature branch of the liquid–liquid–vapor curve for the binary system $CClF_3$ + dodecane is prevented by the occurrence of a solid phase and that $CClF_3$ + dodecane is basically a type IV system.

In Fig. 9 the temperatures of the LCEP $L_2 = L_1 + V$ and the UCEP $L_2 + L_1 = V$ of binary ethene + n-alkane systems are plotted. The liquid–liquid–vapor pressure as a function of temperature for these systems is given in Table VI. In this family no liquid–liquid–vapor equilibria are found for ethene + tridecane. The systems of ethene + n-alkanes with carbon numbers 14–17 show type V phase behavior. However, in view of

Table V. Temperature and Pressure of the Quadruple-Point Solid–Liquid–Liquid–Vapor in the $CClF_3 + n$-Alkane Family at a Given Average Carbon Number n of the n-Alkane

n	T (K)	P (MPa)
12.1007	254.03	1.160
12.2007	251.26	1.052
12.3751	251.10	1.082

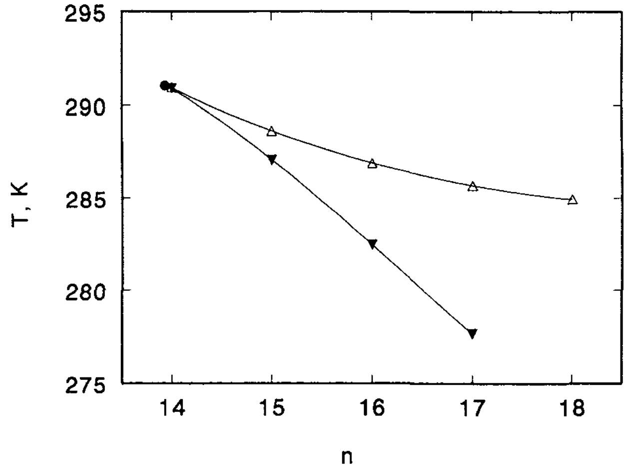

Fig. 9. The family of ethene + *n*-alkanes: critical endpoint temperature as a function of the average carbon number *n* of the *n*-alkane. (▼) LCEP $L_2 = L_1 + V$; (△) UCEP $L_2 + L_1 = V$; (●) tricritical point.

Table VI. Liquid-Liquid-Vapor Equilibrium Pressure in Binary Ethene + *n*-Alkane Systems

T (K)	P (MPa)
Ethene + tetradecane	
290.91	5.885[a]
290.95	5.890[b]
Ethene + pentadecane	
287.06	5.425[a]
287.40	5.470
287.62	5.500
287.96	5.545
288.19	5.575
288.43	5.605
288.62	5.630[b]
Ethene + octadecane	
282.30	4.962
283.51	5.102
284.50	5.220
284.94	5.272[b]

Table VI. *(Continued)*

T (K)	P (MPa)
Ethene + hexadecane	
282.45	4.925[a]
282.91	4.980
283.26	5.020
283.81	5.085
284.34	5.150
284.86	5.210
285.35	5.270
285.90	5.335
286.31	5.385
286.61	5.425
286.88	5.460[b]
Ethene + heptadecane	
277.67	4.450[a]
277.81	4.460
278.10	4.490
278.38	4.520
278.71	4.555
279.20	4.605
280.19	4.710
281.16	4.820
282.19	4.940
283.20	5.500
284.14	5.160
285.20	5.285
285.69	5.345[b]

[a] LCEP $L_2 = L_1 + V$.
[b] UCEP $L_2 + L_1 = V$.

the experimental findings for the family of $CClF_3$ + n-alkanes, it is possible and even likely that also in this family the low-temperature branch of the liquid–liquid–vapor curve is hidden below the solidification surface and that these systems are really type IV systems. In the system ethene + octadecane no LCEP $L_2 = L_1 + V$ is found because of solidification of solid octadecane. In the system ethene + eicosane, the complete liquid–liquid–vapor curve is hidden below the solidification surface, as shown by Gregorowicz et al. [20]. For this family we find $n_{\mathrm{TCP}} = 13.93$ and $T_{\mathrm{TCP}} = 291.0$ K. The liquid–liquid–vapor curve in the system ethene + tetradecane is only 0.04 K long. So this binary system is very close to tricriticality.

4. CONCLUSIONS

Our studies of the fluid phase behavior of families of high-volatile components with *n*-alkanes and *n*-alkane mixtures support the idea that increasing the carbon number of the *n*-alkane practically always leads to a transition from type II to type IV to type III fluid phase behavior. Although some systems may appear to deviate from this trend, it may be the occurrence of solid phases which obscures it. The only exception to this rule may be for the family of water + *n*-alkanes [21].

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