Registry No. DMF, 68-12-2; *p*-xylene, 106-42-3; ethylbenzene, 100-41-4.

Literature Cited

(1) Vogel, A. I. *A Textbook of Practical Organic Chemistry Including Qualitative Organic Analysis*, 3rd ed.; Longmans: London, 1959.
(2) Sood, B. K.; Bagga, O. P.; Raju, K. S. N. *J. Chem. Eng. Data* **1972**, *17*, 435.
(3) Timmermans, J. *Physico-Chemical Constants of Pure Organic Compounds*; Elsevier: Amsterdam, 1965; Vol. II.
(4) Lange, N .A., Ed. *Handbook of Chemistry*, revised 10th ed.; McGraw-Hill: New York, 1967.
(5) Gallant, R. W. *Hydrocarbon Process.* **1969**, *48*(6), 141.
(6) Raju, B. N.; Ranganathan, R.; Rao, M. N. *Indian Chem. Eng.* **1965**, *7*, T33.
(7) Benedict, M., Johnson, C. A., Solomon, E., Rubin, L. C. *Trans. Am. Inst. Chem. Eng.* **1945**, *41*, 371.
(8) Mertes, T. S., Colburn, A. P. *Ind. Eng. Chem.* **1947**, *39*, 787.
(9) Mittal, S. M. S. Chemical Engineering Thesis, Panjab University, Chandigarh, India, 1972.
(10) Miller, D. G. *J. Phys. Chem.* **1965**, *69*, 3209.
(11) O'Connell, J. P.; Prausnitz, J. M. *Ind. Eng. Chem. Process Des. Dev.* **1967**, *6*, 245.
(12) Pitzer, K. S.; Curl, R. F. *J. Am. Chem. Soc.* **1957**, *79*, 2369.
(13) Goldhammer, C. *Z. Phys.* **1910**, *71*, 577.
(14) Herrington, E. F. G. *Nature (London)* **1947**, *160*, 610.
(15) Herrington,, E. F. G. *J. Inst. Pet.* **1951**, *37*, 457.
(16) Black, C. *Ind. Eng. Chem.* **1958**, *50*, 391.
(17) Black, C. *Ind. Eng. Chem.* **1958**, *50*, 403.
(18) Norrish, R. S.; Twigg, G. H. *Ind. Eng. Chem.* **1954**, *46*, 201.
(19) Carlson, N. C.; Colburn, A. P. *Ind. Eng. Chem.* **1942**, *34*, 581.
(20) Orye, R. V.; Prausnitz, J. M. *Ind. Eng. Chem.* **1965**, *57*, 18.
(21) Redlich, O.; Kister, A. T. *Ind. Eng. Chem.* **1948**, *40*, 345.

Received for review May 6, 1986. Accepted September 30, 1986.

Liquid–Liquid–Vapor Equilibria Behavior of Certain Ethane + *n*-Paraffin Mixtures

Susana S. Estrera and Kraemer D. Luks*
Department of Chemical Engineering, University of Tulsa, Tulsa, Oklahoma 74104

Liquid–liquid–vapor phase equilibria for the binary mixtures ethane + *n*-docosane, *n*-tricosane, and *n*-tetracosane were studied and compared with earlier studies in the literature for the mixtures containing *n*-docosane and *n*-tetracosane. Solid–liquid–vapor phase equilibria were also studied for these binary mixtures. Compositions and molar volumes of the liquid phases in all the multiphase systems are reported. The study indicates a transition in the nature of the liquid–liquid–vapor locus between *n*-tricosane and *n*-tetracosane.

Introduction

There has been interest in the liquid–liquid–vapor (LLV) phase equilibria behavior of ethane with the homologous series of *n*-paraffins. Following up earlier studies of Kohn et al. (*1*), Specovius et al. (*2*) established that LLV immiscibility commences with *n*-octadecane and continues through at least *n*-eicosane. The LLV loci are terminated from below by a lower critical end point (LCEP, or L=L–V) and from above by a K point (L–L=V), often known as an upper critical end point (UCEP). Rodrigues and Kohn (*3*) identified similar LLV behavior for the mixture ethane + *n*-docosane, with the extent of the LLV locus increasing with the carbon number of the *n*-paraffin; although the K point moves slightly lower in temperature with increasing carbon number, the LCEP moves substantially lower at the same time.

In a little-known study, Patel (*4*) reported the behavior along the LLV locus for the mixture ethane + *n*-tetracosane. This locus differed from those of the lighter *n*-paraffins in that its lower terminus was a quadruple point (Q point, or SLLV), as would be expected with further increase of the carbon number. The Q point marks the intersection of the SLV locus with the LLV locus; since the SLV locus originates at the triple point of the heavy hydrocarbon, it will move upward in temperature with increasing carbon number, eventually intersecting the LLV locus. LLV immiscibility is finally lost with increasing carbon number when the SLV locus follows a path temperaturewise above the (potential) K point. The reader is referred to ref *5* for a discussion of the topography of multiphase systems in thermodynamic phase space.

In this paper we will report on the LLV behavior of ethane + *n*-docosane, *n*-tricosane, and *n*-tetracosane. The investigators have attempted to update the earlier studies on *n*-docosane and *n*-tetracosane, using components of improved purity. Peters et al. (*6*) recently reported some results (plots only) for the SLV loci of this homologous series, identifying *n*-tetracosane as the first *n*-paraffin to display a Q(SLLV) point. Our results herein confirm this.

Experimental Apparatus and Procedure

A detailed description of the experimental apparatus is given in an earlier paper by Fall and Luks (*7*). The procedure for performing LLV studies is presented by Fall et al. (*8*). The apparatus employs a stoichiometric approach wherein a known amount of *n*-paraffin is added to a visual (glass) equilibrium cell. (The volume of these cells is typically 7–8 mL.) Measured amounts of ethane gas are added to the cell from a high-pressure bomb. By careful mass balances, the moles of ethane in the liquid phases can be determined from "conjugate" measurements at a given temperature. Conjugate measurements involve two experimental runs in which one measurement has a large amount of L_1 relative to L_2 present. The second measurement has L_2 in excess. The vapor phase in all experiments is kept small and is assumed to be pure ethane due to the low volatility of the *n*-paraffins at the temperatures of interest. The termination points of the LLV loci are determined individually by straightforward visual observation.

Determination of a solid–liquid–vapor point is done by cooling a vapor–liquid system until crystals form and then slowly heating up the agitated system until only a trace of crystals remain. This procedure, combined with the vapor-phase assumptions stated above, permits determination of the liquid composition and molar volume, although care must be taken to ensure thermal and chemical equilibria at the crystal point.

Temperature is measured with a Pt-resistance thermometer to an estimated accuracy of ±0.02 K. Pressure is measured to ±0.07 bar with pressure transducers which are frequently

0021-9568/87/1732-0201$01.50/0

Table I. Raw Data for the LLV Locus of the Binary System Ethane + n-Docosane

		L_1 phase		L_2 phase	
temp, °C	press., bar	$[C_2]$, mole fracn	molar vol, mL/(g mol)	$[C_2]$, mole fracn	molar vol, mL/(g mol)
28.31	44.55[a]				
29.61	45.62	0.9414	90.3	0.9878	87.2
29.87	45.85	0.9392	91.0	0.9912	87.6
31.48	47.49	0.9303	93.5	0.9944	91.3
31.96	47.96	0.9283	93.8	0.9948	93.5
33.18	49.25	0.9227	95.6	0.9963	97.6
33.96	50.09	0.9192	96.8	0.9975	100.4
35.06	51.48[b]				

[a] LCEP (L=L-V). [b] K point (L-L=V).

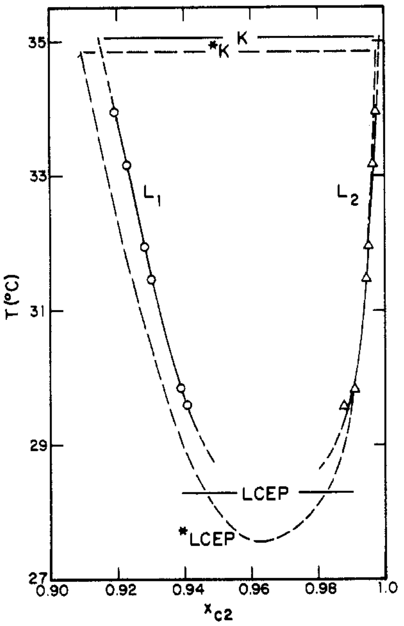

Figure 1. Composition as a function of temperature for the L_1 and L_2 phases for the liquid-liquid-vapor locus of ethane + *n*-docosane. (The dashed lines and asterisks refer to the smoothed data of ref *3*.)

Table II. Raw Data for the LLV Locus of the Binary System Ethane + n-Tricosane

		L_1 phase		L_2 phase	
temp, °C	press., bar	$[C_2]$, mole fracn	molar vol, mL/(g mol)	$[C_2]$, mole fracn	molar vol, mL/(g mol)
25.00	41.39[a]				
25.79	42.11	0.9463	89.3	0.9848	85.5
26.01	42.28	0.9440	89.2	0.9862	85.4
26.49	42.75	0.9411	90.5	0.9882	86.2
26.79	43.01	0.9376	90.3	0.9895	86.3
27.39	43.58	0.9364	91.4	0.9901	85.7
28.42	44.56	0.9309	92.8	0.9922	87.2
28.78	44.88	0.9264	92.5	0.9937	89.4
29.67	45.75	0.9226	93.0	0.9951	91.4
30.38	46.48	0.9222	95.3	0.9953	91.0
31.37	47.50	0.9186	96.5	0.9967	94.3
32.37	48.53	0.9142	98.2	0.9978	98.4
33.73	49.96	0.9095	99.3	0.9982	105.3
34.35	50.67[b]				

[a] LCEP (L=L-V). [b] K point (L-L=V).

Table III. Raw Data for the LLV Locus of the Binary System Ethane + n-Tetracosane

		L_1 phase		L_2 phase	
temp, °C	press., bar	$[C_2]$, mole fracn	molar vol, mL/(g mol)	$[C_2]$, mole fracn	molar vol, mL/(g mol)
28.56	44.75[a]				
29.14	45.38	0.9169	97.5	0.9948	92.0
29.49	45.72	0.9159	97.6	0.9956	92.6
30.07	46.30	0.9136	98.2	0.9963	94.1
30.91	47.15	0.9111	98.9	0.9971	96.5
31.32	47.55	0.9100	99.6	0.9977	97.8
32.25	48.50	0.9083	99.8	0.9990	101.3
32.68	48.95	0.9050	101.3	0.9993	105.2
33.18	49.47	0.9033	102.1	0.9996	109.6
33.99	50.34[b]				

[a] Q point (SLLV). [b] UCEP (L-L=V).

Table IV. Temperature, Pressure, Liquid-Phase Composition, and Molar Volume Raw Data for the Solid-Liquid-Vapor Locus of Ethane + n-Docosane

temp., °C	press., bar	$[C_2]$, mole fracn	molar vol, mL/(g mol)
43.70	1.01[a]		
39.53	11.09	0.3455	275.1
34.17	23.27	0.6054	190.8
30.25	30.38	0.7209	145.8
27.95	33.54	0.7772	134.6
23.68	37.25	0.8682	103.1
22.12	37.98	0.9133	94.7

[a] Air-saturated melting point.

calibrated with a dead-weight gauge. Phase volumes in the calibrated visual cell are determined by a cathetometer to an accuracy of ±0.005 mL.

Materials

The *n*-docosane, *n*-tricosane, and *n*-tetracosane were purchased from Alfa Products with a stated purity of 99%. Their melting points were determined to be 43.7 ± 0.1, 47.6 ± 0.1, and 51.4 ± 0.1 °C, respectively. These values compare favorably with those found in the literature (*9*, *10*). Chromatographic analyses of solutions of these *n*-paraffins in decane suggest that their purity is better than 99 mol %.

The ethane was obtained from the Matheson Co. as a Research Purity Grade gas with a minimum rating of 99.99 mol %. The difference between the bubble point and dew point at 25 °C was about 1 psi, and the vapor pressure was within ±1 psi of the literature value (*11*).

No further purification of the *n*-paraffins or the ethane was performed.

Results

Table I presents raw data for the LLV locus of the mixture ethane + *n*-docosane, including composition and molar volume for each of the liquid phases present. Figures 1 and 2 show the L_1 and L_2 compositions and molar volumes plotted against temperature as found in Table I. Also shown are the smoothed results of Rodrigues and Kohn (*3*) for this same mixture. The mole fractions should be good to ±0.001 and the molar volumes should be good to ±0.6 mL/(g mol). These are conservative estimates, based on the averge absolute deviations (AAD) of the raw data from the smoothed curves (drawn by eye) shown in the figures. They are offered here as appropriate to the data in Tables I–III. The AAD's for the ethane compositions in both liquid phases for the different LLV studies were always less than or equal to 0.001 while the corresponding AAD's for the molar volumes ranged from 0.1 to 0.5 mL/(g mol).

Table II presents raw data for the mixture ethane + *n*-tricosane along its LLV locus, while Figures 3 and 4 show the L_1 and L_2 compositions and molar volumes plotted against temperature. Table III contains the raw data for the mixture ethane + *n*-tetracosane along its LLV locus, while Figures 5 and 6 show the liquid-phase compositions and molar volumes plotted against temperature. Also shown in Figures 5 and 6 are the smoothed data of Patel (*4*).

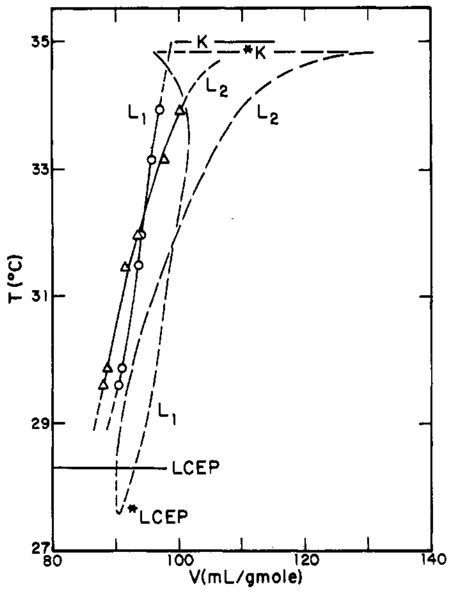

Figure 2. Molar volume as a function of temperature for the L_1 and L_2 phases for the liquid–liquid–vapor locus of ethane + *n*-docosane. (The dashed lines and asterisks refer to the smoothed data of ref *3*.)

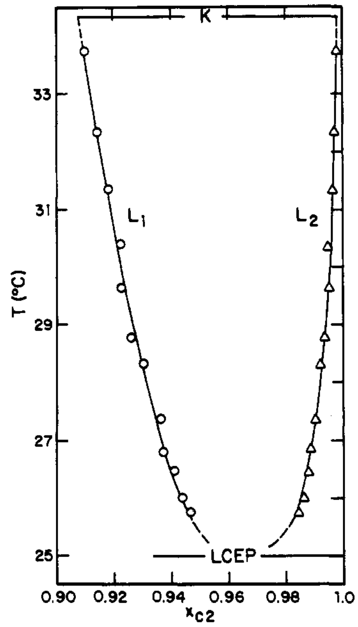

Figure 3. Composition as a function of temperature for the L_1 and L_2 phases for the liquid–liquid–vapor locus of ethane + *n*-tricosane.

Table V. Temperature, Pressure, Liquid-Phase Composition, and Molar Volume Raw Data for the Solid–Liquid–Vapor Locus of Ethane + *n*-Tricosane

temp, °C	press., bar	[C_2], mole fracn	molar vol, mL/(g mol)
47.61	1.01[a]		
44.12	7.40	0.2518	315.6
40.74	14.21	0.4081	256.5
37.42	20.26	0.5229	225.5
33.84	27.74	0.6511	181.8
32.68	29.83	0.6855	171.2
31.50	31.89	0.7181	161.0
28.77	35.74	0.7864	138.2
26.67	37.97	0.8364	121.2
24.76	39.33	0.8827	107.1
24.00	39.40	0.8992	98.7
22.81	39.42	0.9687	85.2
22.43	39.14	0.9825	85.3

[a] Air-saturated melting point.

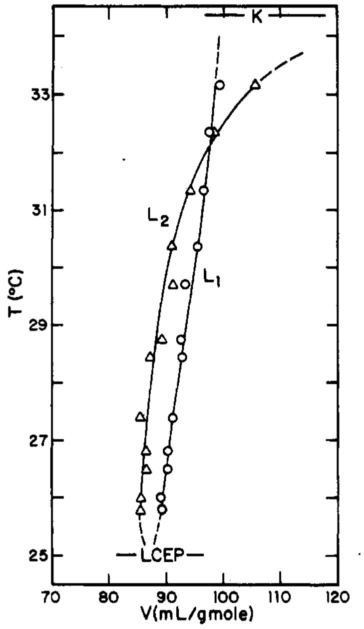

Figure 4. Molar volume as a function of temperature for the L_1 and L_2 phases for the liquid–liquid–vapor locus of ethane + *n*-tricosane.

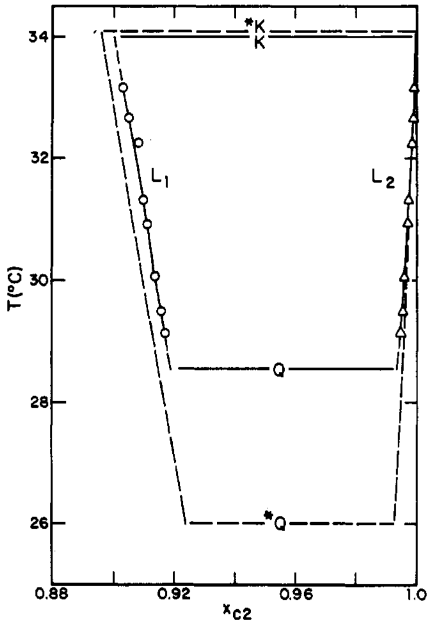

Figure 5. Composition as a function of temperature for the L_1 and L_2 phases for the liquid–liquid–vapor locus of ethane + *n*-tetracosane. (The dashed lines and asterisks refer to the smoothed data of ref *4*.)

Table VI. Temperature, Pressure, Liquid-Phase Composition, and Molar Volume Raw Data for the Solid–Liquid–Vapor of Ethane + *n*-Tetracosane

temp, °C	press., bar	[C_2], mole fracn	molar vol, mL/(g mol)
51.43	1.01[a]		
47.85	8.44	0.2609	331.1
44.94	14.14	0.4102	273.8
44.40	15.87	0.4384	261.6
39.91	28.15	0.6279	195.6
36.61	34.64	0.7219	162.9
33.09	40.27	0.8022	135.9
28.56	44.75[b]		

[a] Air-saturated melting point. [b] Q point (SLLV).

Tables IV–VI list the raw data for the SLV loci of ethane + *n*-docosane, *n*-tricosane, and *n*-tetracosane, respectively. These loci extend from the air-saturated melting point (roughly

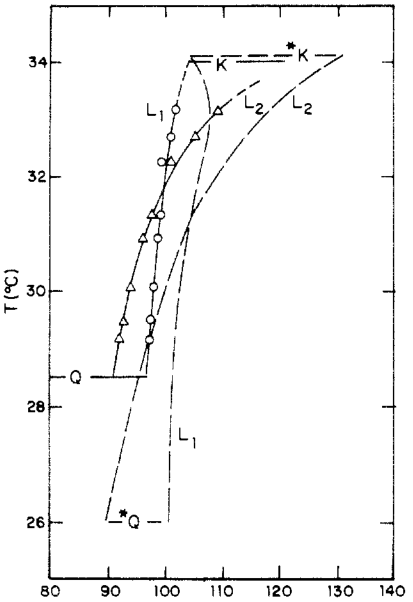

Figure 6. Molar volume as a function of temperature for the L_1 and L_2 phases for the liquid–liquid–vapor locus of ethane + *n*-tetracosane. (The dashed lines and asterisks refer to the smoothed data of ref *4*.)

the same temperature as the triple point) upward in pressure (downward in temperature). For *n*-docosane and *n*-tricosane, the locus goes through a pressure maximum, while for *n*-tetracosane it terminates at the Q point, the lower terminus of the LLV locus. The liquid-phase compositions are estimated to be good to ±0.003 while the liquid molar volumes should be good to ±1.0 mL/(g mol). These estimates are, as before, based on AAD's determined from placing smoothed curves (not shown) through the raw data in the tables. Actual AAD's for the liquid-phase properties were somewhat lower than these estimates. The determination of SLV data is more difficult than that of LLV data, resulting in larger uncertainties in the liquid-phase properties.

Remarks

There are some minor discrepancies between our LLV results on ethane + *n*-docosane and ethane + *n*-tetracosane and those of Rodrigues and Kohn (*3*) and Patel (*4*), respectively. Most obvious are the differences in the lower termini of the LLV loci. For example, the Q point of Patel is more than 2 °C lower. A rough estimate of the Q-point temperature of Peters et al. (*6*) is about 28.4 °C, or within 0.2 °C of our result in Table III. A possible explanation of the discrepancy is greater impurity in Patel's *n*-tetracosane, resulting in depression of the SLV locus, including the Q point. A similar explanation could account for the discrepancy between LCEP's (Figures 1 and 2) for ethane + *n*-docosane. The earlier studies used *n*-paraffins with stated purities of 97 mol %, without further purification. They also upgraged ethane from stated purities of 99 mol %, using in-house purification techniques, but the difference claimed between bubble and dew point pressures was at least 3 psi.

By documenting the behavior of the mixture ethane + *n*-tricosane along the SLV locus, it is established that the mixture has an LLV locus like that of the lighter *n*-paraffins, e.g., *n*-octadecane to *n*-docosane. With *n*-tetracosane, the LLV locus is able to reach the SLV locus, in agreement with the SLV results of Peters et al. (*6*). Although the possibility existed, there occurs no mixture in the homologous series exhibiting two separate LLV branches, as in the mixtures CO_2 + *n*-tridecane (*12*, *13*) and CO_2 + *n*-heptylbenzene (*14*). Table VII lists the end points of the LLV loci for the homologous series of ethane + *n*-paraffins.

Table VII. LLV Loci End Points for Ethane + *n*-Paraffin Systems

carbon	this study		literature		
no.	press., bar	temp, °C	press., bar	temp, °C	ref
18			55.11[a]	39.14	*2*
			55.31[b]	39.30	
19			52.11[a]	36.34	*2*
			53.63[b]	37.63	
20			49.27[a]	33.54	*2*
			52.60[b]	36.47	
22	44.55[a]	28.31	43.88	27.57	*3*
	51.48[b]	35.06	51.45	34.83	
23	41.39[a]	25.00			
	50.67[b]	34.35			
24	44.75[c]	28.56	42.77	26.00	*4*
	50.34[b]	33.99	50.23	34.09	

[a] LCEP (L=L–V). [b] K point (L–L=V). [c] Q point (SLLV).

Finally, the question arises as to where immiscibility ends in the homologous series. Peters et al. (*6*) have suggested that *n*-pentacosane is the last member of the series to exhibit LLV behavior, by virtue of the existence of a Q point interrupting the SLV locus. We were unable to acquire a pure enough sample of *n*-pentacosane to confirm or deny this result; however, some preliminary results of ours with *n*-hexacosane agree with those of Peters et al. (*6*), and it seems likely that *n*-pentacosane will have a small LLV locus.

Glossary

AAD	average absolute deviation
K	a K point, a critical end point where L–L=V
L, L_1, L_2	liquid phases
L–L=V	a three-phase critical end point where L and V are critically identical
L=L–V	a three-phase critical end point where the two liquid phases are critically identical
LCEP	a lower critical end point where L=L–V
Q	a Q point, or quadruple point, which has four phases in equilibria; herein, the four phases are SLLV
S	solid phase
V	vapor phase

Literature Cited

(1) Kohn, J. P.; Kim, Y. J.; Pan, Y. C. *J. Chem. Eng. Data* **1966**, *11*, 333–335.
(2) Specovius, J.; Leiva, M. A.; Scott, R. D.; Knobler, C. M. *J. Phys. Chem.* **1981**, *85*, 2313–2316.
(3) Rodrigues, A. B.; Kohn, J. P. *J. Chem. Eng. Data* **1967**, *12*, 191–193.
(4) Patel, A. D. M.S. Thesis, University of Notre Dame, Aug. 1966.
(5) Luks, K. D.; Kohn, J. P. *Proceedings of the 63rd Annual Convention Gas Processors Association, New Orleans, LA, March 21, 1984*; Gas Processors Association: Tulsa, OK, 1984. pp 181–6.
(6) Peters, C. J.; Lichtenthaler, R. N.; de Swaan Arons, J. *Fluid Phase Equilib*. **1986**, *29*, 495–504.
(7) Fall, D. J.; Luks, K. D. *J. Chem. Eng. Data* **1984**, *29*, 413–417.
(8) Fall, D. J.; Fall, J. L.; Luks, K. D. *J. Chem. Eng. Data* **1985**, *30*, 82–88.
(9) Perry, R. H.; Chilton, C. H. *Chemical Engineers' Handbook*, 5th ed.; McGraw-Hill: New York, 1975; pp 3-25–44.
(10) Weast, R. C. *Handbook of Chemistry and Physics*, 51st ed.; The Chemical Rubber Co.: Boca Raton, FL, 1970; pp C53–542.
(11) Douslin, D. R.; Harrison, R. H. *J. Chem. Thermodyn.* **1973**, *5*, 491–512.
(12) Fall, D. J.; Luks, K. D. *J. Chem. Eng. Data* **1985**, *30*, 276–279.
(13) Enick, R.; Holder, G. D.; Morsi, B. I. *Fluid Phase Equilib*. **1985**, *22*, 209–224.
(14) Fall, J. F.; Luks, K. D. *Fluid Phase Equilib*. **1986**, *28*, 87–96.

Received for review May 28, 1986. Support of this research was provided by The National Science Foundation (Grant No. CBT-8514599). Accepted December 8, 1986. The apparatus used is part of the PVTx Laboratory at The University of Tulsa and was purchased with funds provided by several industries, The University of Tulsa, and a National Science Foundation specialized equipment grant (No. CPE-8104650).