Double Azeotropy in Binary Mixtures 1,1,1,2,3,4,4,5,5,5-Decafluoropentane + Tetrahydrofuran

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Vapor−liquid equilibria have been measured as a function of overall composition for binary mixtures of 1,1,1,2,3,4,4,5,5,5-decafluoropentane (HFC-4310mee) + tetrahydrofuran (THF) at 323.18 K using a static cell and at 26.68 kPa and 58.58 kPa using an ebulliometer. The data were correlated using the NRTL equation. The coexistence curves at 26.68 kPa exhibit a maximum and a minimum in temperature, establishing the existence of double azeotropes at this pressure.

Introduction

Binary double azeotropy is an unusual vapor−liquid equilibrium (VLE) phenomenon where two stable azeotropes exist at a given temperature or pressure. Wisniak et al.[1] made a thermodynamical analysis of polyazeotropy for binary systems at low pressures and established the necessary and sufficient conditions that provoke it. Double azeotropes have been found for four organic binary mixtures: benzene and hexafluorobenzene,[2,3] diethylamine and methanol,[4,5] acetic acid and isobutyl acetate,[6,7] and ammonia and pentafluoroethane or HFC-125.[8] The double azeotropy for ammonia and HFC-125 is unusual in that they exist at temperatures for which the vapor pressures of the components are notably different. The large difference between the vapor and liquid compositions at the ammonia end was not found in the other three binary systems. Leu and Robinson[9] reported that 1,2-butylene oxide and methyl acetate exhibited two azeotropes at 298.15 K. However, Monton et al.[10] measured the VLE for the same system at 35 and 101.3 kPa and at 298.15 K and found no azeotropes. Monton et al.[10] claimed the data of Leu and Robinson[9] were in error because of impurities in the reagents and experimental errors.

Binary VLE data for HFC-4310mee and THF were measured at 323.18 K using a static cell. The data at the THF end suggested the mixture might have two azeotropes. The system was remeasured at 26.68 kPa and 58.58 kPa using an ebulliometer. The data were correlated using the NRTL equation. The coexistence curves at 26.68 kPa exhibited a maximum and a minimum in temperature, establishing the existence of double azeotropes at this pressure.

Experimental Section

THF with purity >99.9% was purchased from Aldrich. HFC-4310mee with purity 99.92% was manufactured by DuPont. Both compounds were used without further purification; however, both were degassed prior to making the measurements using a static cell.

Static Cell. In a static cell one measures equilibrium pressure for a mixture of known composition at a constant temperature. The static cell apparatus and procedures for VLE measurements for compounds of normal boiling points below ambient temperature were described previously.[8,11] The normal boiling points for both HFC-4310mee and THF were above ambient temperature; different methods were used to degas the pure compounds and to prepare mixtures. Approximately 35 g of HFC-4310mee was drawn into an evacuated 85 cm^3 stainless steel equilibrium cell, which had an injection port the same as that of a HP 5890A gas chromatograph. This compound was degassed while the cell was immersed in an ultrasonic bath at 50 °C. Vapor pressure was measured to verify thorough degassing. THF was poured into a 30 cm^3 glass vial, the vial was then capped with a septum. The THF in the glass vial was degassed with a needle through the septum while the vial was immersed in a ultrasonic bath at 50 °C. Mixtures were prepared by injecting known masses of the THF in the glass vial into HFC-4310mee in the stainless steel equilibrium cell using a gastight syringe. The added quantities (ranging from approximately 0.6 to 3.3 g) were determined to 0.001 g by weighing the syringe. Successive isothermal equilibrium pressure measurements for the binary mixture were made over roughly half of the composition range. Equilibrium pressures over the other half of the composition range were obtained by repeating the procedure starting with approximately 23 g of THF in the equilibrium cell and adding 3.2 to 4.8 g of the HFC-4310mee each time.

Ebulliometer. An ebulliometer measures equilibrium temperature for a mixture at a controlled pressure. A single boiler (Figure 1) was used for this work; it was a smaller version of the one designed by Scott.[12] The volume of the boiler was 221 cm^3, with a 0.2 cm^3 liquid holdup. The liquid holdup was determined by comparing binary ethanol + *n*-heptane VLE data at 27.58 kPa measured by the 221 cm^3 boiler to those measured by a 924 cm^3 boiler as described in the Appendix. The pressure of the boiler was kept constant by a Mensor PCS 400 pressure controller with 0.01% or 0.01 kPa accuracy, and a Paroscientific 740-16B pressure transducer with 0.01% accuracy was used to measure the pressure of the boiler. The temperature was measured using a Hart Scientific Black Stack Base Unit with 0.007 K accuracy and a secondary PRT with 0.01 K accuracy (ITS-90 scale).

At 58.58 kPa, half of the data were measured by adding approximately 0.8 to 4 g of THF to 40 g of HFC-4310mee; the other half were measured by adding approximately 3

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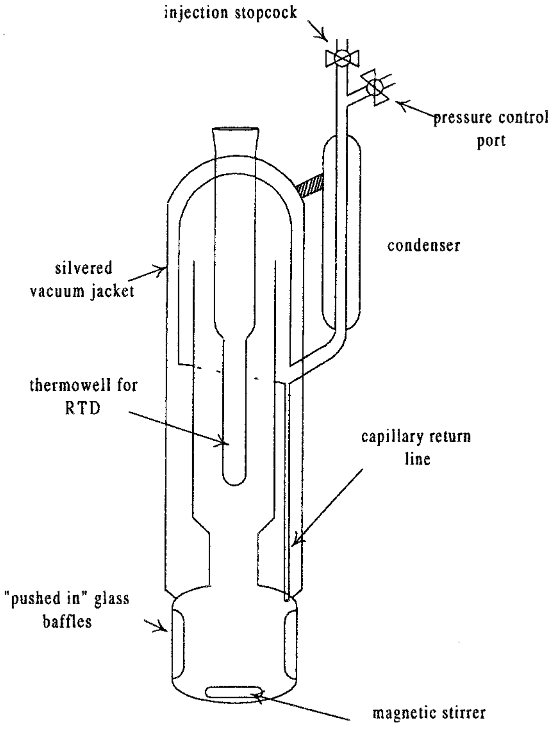

Figure 1. Schematic diagram for the 221 cm^3 boiler.

to 6.4 g of HFC-4310mee to 21 g of THF. At 26.68 kPa, half of the data were measured by adding approximately 0.9 to 4.8 g of THF to 56 g of HFC-4310mee; the other half were measured by adding approximately 2 to 8.6 g of HFC-4310mee to 27.6 g of THF. All the weights were measured to 0.001 g.

Results and Discussion

HFC-4310mee/THF at 323.18 K Measured by a Static Cell. The overall mixture composition, calculated on the basis of known loadings of the two components, was converted to equilibrium vapor- and liquid-phase compositions by accounting for the small amount of each component in the vapor phase as described by Kao et al.[8] However, instead of using the Peng–Robinson equation of state to calculate both vapor and liquid fugacities of each component as described by Kao et al.,[8] the ideal gas law is used for vapor-phase fugacity calcualtions and the NRTL (nonrandom, two-liquid) equation[13] is used for liquid-phase fugacity calculations. The details of data reduction are described in the next section. The NRTL parameters are obtained by minimizing $\{1/N[\sum(P_{\mathrm{calc}}/P - 1)^2]\}^{1/2}$.

The reduced NRTL parameters for HFC-4310mee/THF at 323.18 K are $\alpha_{12} = 0.44$, $\tau_{12}T$ = -434.56 K, and $\tau_{21}T$ = 787.51 K. The measured and calculated vapor–liquid equilibrium pressures and phase compositions are given in Table 1 and Figure 2. The binary HFC-4310mee/THF system shows asymmetrical phase behavior; that is, the phase behavior at the HFC-4310mee end is quite different from the phase behavior at the THF end. The pressure decreases sharply and the vapor compositions are quite different from the liquid compositions at the HFC-4310mee end. The pressure increases slightly, and vapor and liquid coexistence curves are close to showing an inflection point, corresponding to a saddle point azeotrope at the THF end. The behavior at the THF end suggests this mixture might have two azeotropes. Since our static cell is not designed to measure VLE at pressures lower than 50 kPa, an ebulliometer was used to remeasure the VLE for this binary.

Table 1. Vapor–Liquid Equilibrium Pressures and Phase Compositions for HFC-4310mee (1) + THF (2) Mixtures at 323.18 K

X_2	$Y_{2,\mathrm{calc}}$	P/kPa	P_{calc}/kPa	$(P_{\mathrm{calc}} - P)/P$
0.000	0.0000	86.94	86.94	
0.0548	0.0240	83.63	84.08	0.005
0.1066	0.0506	81.38	81.36	0.000
0.2061	0.1142	76.70	76.21	−0.006
0.3045	0.1958	71.58	71.44	−0.002
0.4028	0.2974	67.33	67.27	−0.001
0.5023	0.4183	63.89	63.93	0.001
0.5514	0.4826	62.42	62.67	0.004
0.8485	0.8429	60.00	59.88	−0.002
0.8933	0.8855	59.80	59.74	−0.001
0.9264	0.9165	59.58	59.55	0.000
0.9618	0.9521	59.06	59.20	0.002
1.0000	1.0000	58.43	58.43	

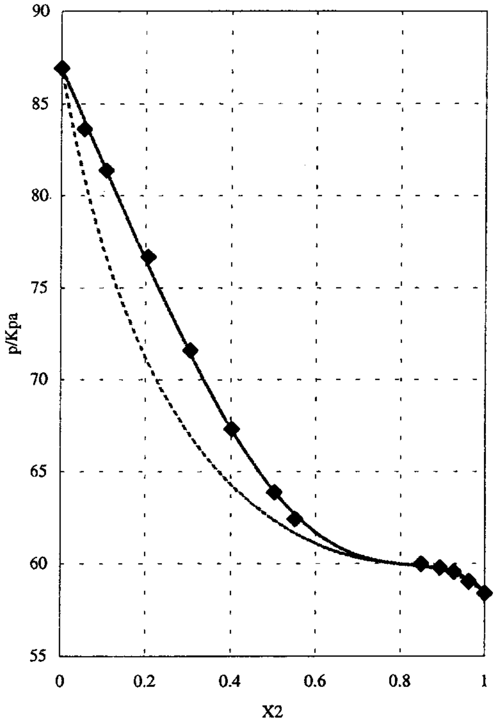

Figure 2. Vapor–liquid equilibrium pressures and phase compositions for HFC-4310mee (1) + THF (2) at 323.18 K. The symbols denote measured pressures. The solid and broken lines are the calculated liquid and vapor coexistence curves, respectively.

HFC-4310mee/THF at 58.58 kPa and 26.68 kPa Measured by an Ebulliometer. Reduction of VLE data measured by an ebulliometer is more complicated than reduction of VLE data measured by a static cell because liquid holdup needs to be taken into account. The material balance equations for reduction of data measured by an ebulliometer are

$$n^{\mathrm{L}} + n^{\mathrm{V}} + n^{\mathrm{cond}} = n_1 + n_2 \tag{1}$$

$$n_1 = x_1 n^{\mathrm{L}} + y_1 n^{\mathrm{V}} + y_1 n^{\mathrm{cond}} \tag{2}$$

$$V_{\mathrm{T}} = n^{\mathrm{L}} v^{\mathrm{L}} + n^{\mathrm{V}} v^{\mathrm{V}} + V^{\mathrm{cond}} \tag{3}$$

where n_i is the number of moles of component i charged to the boiler, n^{α} is the total number of moles in phase α, v^{α} is the molar volume of phase α, x_1 and y_1 are the liquid and vapor mole fractions of component 1, V^{cond} is the volume of

Table 2. Vapor−Liquid Equilibrium Temperatures and Phase Compositions for HFC-4310mee (1) + THF (2) at 58.58 KPa

X_2	$Y_{2,\mathrm{calc}}$	T/K	T_{calc}/K	$(T_{\mathrm{calc}} - T)$/K
0.0000	0.0000	312.52	312.52	0.002
0.0678	0.0301	313.55	313.57	0.017
0.1436	0.0718	314.73	314.80	0.067
0.2147	0.1199	315.89	315.98	0.094
0.3271	0.2160	317.77	317.85	0.086
0.4195	0.3137	319.24	319.27	0.031
0.4934	0.4025	320.30	320.26	−0.042
0.5699	0.5005	321.19	321.09	−0.104
0.7450	0.7232	322.20	322.17	−0.030
0.7958	0.7812	322.32	322.32	0.001
0.8405	0.8288	322.40	322.42	0.022
0.8814	0.8701	322.49	322.52	0.030
0.9152	0.9037	322.60	322.62	0.024
0.9549	0.9446	322.79	322.81	0.016
1.0000	1.0000	323.19	323.19	0.000

the liquid holdup, and V_T is the total volume of the boiler. When there is no liquid holdup, these material balance equations become the same equations used for reduction of data measured by a static cell.[8] An expression for the number of moles in the liquid phase is derived from eqs 1 and 3:

$$n^{L} = [(n_1 + n_2 - n^{\mathrm{cond}})v^{V} + V^{\mathrm{cond}} - V_T]/(v^{V} - v^{L}) \quad (4)$$

v^V, v^L, and n^{cond} (number of moles in liquid holdup) are calculated as

$$v^{V} = RT/P \quad (5)$$

$$v^{L} = x_1 v_1^{L} + x_2 v_2^{L} \quad (6)$$

$$n^{\mathrm{cond}} = V^{\mathrm{cond}}/(y_1 v_1^{L} + y_2 v_2^{L}) \quad (7)$$

where R is the gas constant and v_i^L is the liquid molar volume of pure component i.

The expression for the mole fraction of component 1 in the liquid phase is derived from eqs 1 and 2:

$$x_1 = [n_1 - (n_1 + n_2 - n^{L})y_1]/n^{L} \quad (8)$$

A solution for x_1 is found at the pressure of interest by a conventional vapor−liquid equilibrium calculation in which the equilibrium temperature and y_1 are first determined from the pressure and an initial guess for x_1. In this calculation, the ideal gas law is used for vapor-phase fugacity calculations and the NRTL equation is used for liquid-phase fugacity calculations. The NRTL parameters are obtained by minimizing $\{1/N[\sum(T_{\mathrm{calc}} - T)^2]\}^{1/2}$.

The reduced NRTL parameters for HFC-4310mee/THF at 58.58 kPa and 26.68 kPa are $\alpha_{12} = 0.44$, $\tau_{12}T = -422.17$ K, $\tau_{21}T = 736.27$ K and $\alpha_{12} = 0.44$, $\tau_{12}T = -446.44$ K, $\tau_{21}T = 797.48$ K, respectively. The measured and calculated vapor−liquid equilibrium temperatures and phase compositions are given in Tables 2 and 3 and Figures 3 and 4.

The vapor pressures for HFC-4310mee and for THF used in reducing the two sets of isobaric data are calculated from

$$\ln P/\mathrm{kPa} = 13.61836 - 2267.862/(T/\mathrm{K} - 75) \quad (9)$$

and

$$\ln P/\mathrm{kPa} = 14.55116 - 3020.461/(T/\mathrm{K} - 35) \quad (10)$$

respectively. The constants of these two equations are reduced from the vapor pressure data for pure HFC-4310mee and pure THF listed in Tables 2 and 3 and additional data shown below, which were measured at the same time as the binaries using the same ebulliometer. The measured vapor pressures for HFC-4310mee are 40.34 kPa and 95.86 kPa at 303.60 K and 325.44 K, respectively. The measured vapor pressure for THF is 35.84 kPa at 310.28 K. Equations 9 and 10 are meant to be used to reduce the measured two sets of isobaric VLE data for HFC-4310mee/THF, and are not meant for general usage.

At 58.58 kPa, HFC-4310mee/THF shows asymmetrical phase behavior, which is very similar to that measured in the static cell at 323.18 K. At 26.68 kPa, the coexistence curves exhibit both a maximum and a minimum in temperature, establishing the existence of double azeotropes at this pressure. The double azeotropes are unusual in that they exist at a condition for which the vapor pressures of

Table 3. Vapor−Liquid Equilibrium Temperatures and Phase Compositions for HFC-4310mee (1) + THF (2) at 26.68 KPa

X_2	$Y_{2,\mathrm{calc}}$	T/K	T_{calc}/K	$(T_{\mathrm{calc}} - T)$/K
0.0000	0.000	294.44	294.45	0.005
0.0544	0.0206	295.21	295.23	0.026
0.1003	0.0413	295.84	295.93	0.095
0.1839	0.0883	297.14	297.27	0.132
0.33075	0.1851	299.19	299.32	0.136
0.4089	0.2927	300.86	300.92	0.056
0.4907	0.3970	302.07	302.01	−0.056
0.5579	0.4911	302.82	302.70	−0.126
0.6435	0.6144	303.26	303.23	−0.029
0.6847	0.6717	303.37	303.35	−0.016
0.7304	0.7320	303.38	303.38	0.009
0.7806	0.7924	303.30	303.33	0.033
0.8317	0.8467	303.17	303.21	0.036
0.8806	0.8921	303.06	303.08	0.021
0.9186	0.9242	303.00	303.01	0.006
0.9507	0.9510	302.98	302.98	−0.003
0.9789	0.9768	303.01	303.00	−0.005
1.0000	1.0000	303.08	303.08	−0.007

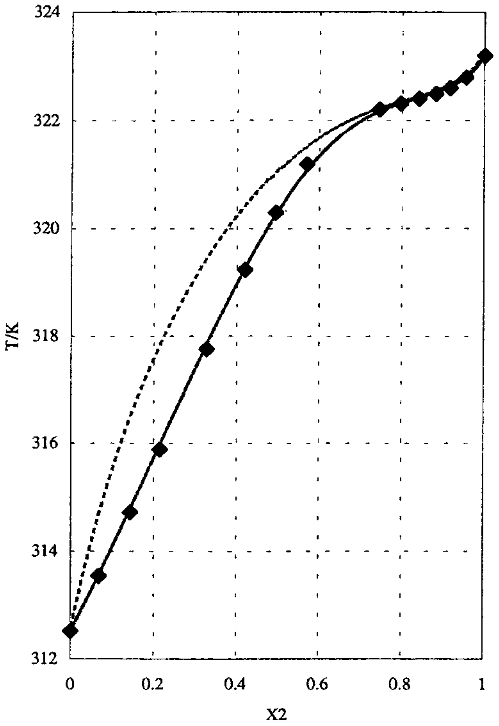

Figure 3. Vapor−liquid equilibrium temperatures and phase compositions for HFC-4310mee (1) + THF (2) at 58.58 kPa. The symbols denote measured pressures. The solid and broken lines are the calculated liquid and vapor coexistence curves, respectively.

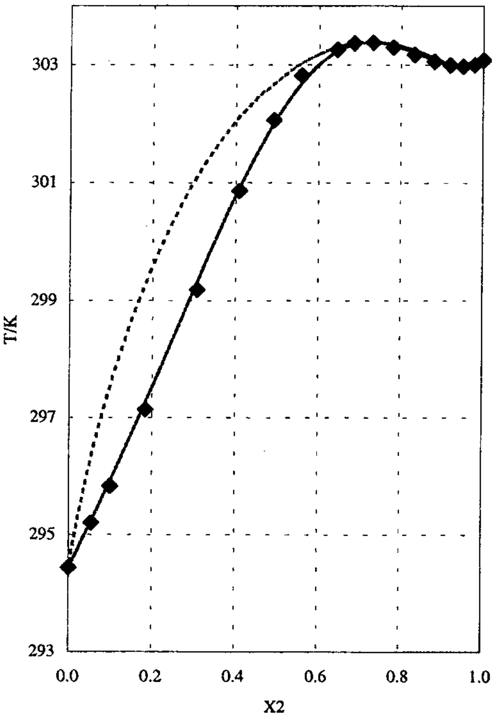

Figure 4. Vapor–liquid equilibrium pressures and phase compositions for HFC-4310mee (1) + THF (2) at 26.68 kPa. The symbols denote measured temperatures. The solid and broken lines are the calculated liquid and vapor coexistence curves, respectively.

the two components are notably different: at 303 K, the vapor pressure for HFC-4310mee is 48% higher than the vapor pressure for THF. There is only one other system in the literature, NH3 and HFC-125,[8] which exhibits double azeotropes at such a condition. Both binaries consist of two very polar components—both NH3 and THF are strong electron donators, while both HFC-125 and HFC-4310mee are strong proton donators. Double azeotropy of both binary systems might result from the cross association between two polar components. The double azeotropy of HFC-4310mee/THF shows another unique property: both azeotropes occur within a narrow temperature and composition range. While the equilibrium temperatures for HFC-4310mee and THF differ by more than 8 K at 26.68 kPa, the difference between the maximum and minimum temperature azeotropes is only 0.4 K. Both azeotropes are concentrated in THF—the mole fractions of THF in azeotropes are approximately 0.73 and 0.95, respectively. For all other double azeotropic binaries, two azeotropes concentrate in two different components and the compositions are approximately symmetrical with respect to equimolar composition. At lower pressures, the maximum temperature azeotrope of HFC-4310mee/THF becomes more prominent, and the minimum temperature azeotrope becomes less notable and finally disappears.

Summary

Vapor–liquid equilibria have been measured as a function of overall composition for binary mixtures of 1,1,1,2,3,4,4,5,5,5-decafluoropentane (HFC-4310mee) and tetrahydrofuran (THF) at 323.18 K using a static cell and at 26.68 kPa and 58.58 kPa using an ebulliometer. The coexistence curves at 26.68 kPa exhibit a maximum and a minimum in temperature, establishing the existence of double azeotropes at this pressure. The double azeotropes are unique in that they exist at a pressure for which the equilibrium temperatures of the two components are notably different and they only cover a narrow temperature and composition range at this pressure.

Table 4. Vapor–Liquid Equilibrium Temperatures and Phase Compositions for Ethanol (1) + n-Heptane (2) at 27.58 kPa Measured by a Boiler of 924 cm^3

X_2	$Y_{2,\mathrm{calc}}$	T/K	T_{calc}/K	($T_{\mathrm{calc}} - T$)/K
0.000 00	0.0000	321.77	321.76	−0.010
0.002 58	0.0194	321.40	321.41	0.007
0.027 85	0.1553	318.80	318.84	0.041
0.066 88	0.1906	318.08	318.13	0.053
0.098 69	0.2634	316.59	316.66	0.067
0.147 96	0.3557	314.76	315.68	0.079
0.203 95	0.3839	314.32	314.84	0.076
0.307 16	0.4106	314.02	314.36	0.037
0.754 30	0.4443	314.29	314.02	0.002
0.905 45	0.4691	315.49	314.19	−0.098
0.955 38	0.5177	317.36	315.09	−0.402
0.975 13	0.5834	319.46	317.08	−0.281
0.984 01	0.6477	321.70	319.69	0.231
0.993 01	0.7774	326.47	322.07	0.374
0.996 42	0.8639	329.18	326.40	−0.077
0.996 73	0.8735	329.51	328.99	−0.194
1.000 00	1.0000	332.70	329.26	−0.253

Table 5. Vapor–Liquid Equilibrium Temperatures and Phase Compositions for Ethanol (1) + n-Heptane (2) at 27.58 kPa Measured by a Boiler of 221 cm^3

X_2	$Y_{2,\mathrm{calc}}$	T/K	T_{calc}/K	($T_{\mathrm{calc}} - T$)/K
0.00000	0.0000	321.77	321.76	−0.010
0.01481	0.0955	319.44	320.00	0.554
0.02985	0.1631	318.09	318.68	0.592
0.06889	0.2672	316.13	316.58	0.454
0.09871	0.3118	315.35	315.68	0.332
0.14889	0.3563	314.63	314.83	0.193
0.19913	0.3820	314.28	314.39	0.108
0.76253	0.4448	314.37	314.21	−0.160
0.91160	0.4721	315.82	315.21	−0.615
0.95663	0.5203	317.56	317.19	−0.372
0.97509	0.5832	319.69	319.68	−0.010
0.98534	0.6612	322.52	322.55	0.029
0.99212	0.7595	325.97	325.83	−0.137
0.99530	0.8319	328.15	328.05	−0.090
1.00000	1.0000	332.70	332.68	−0.020

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Appendix

A boiler smaller than that originally designed by Scott[12] was constructed such that less material would be needed for vapor–liquid equilibrium measurements. The liquid holdup affects the final reduced results more when a smaller boiler is used, and hence needs to be determined accurately. The liquid holdup of the small boiler was determined by comparing the ethanol + n-heptane data measured by two boilers at the same pressure. The results are given in Tables 4 and 5 and Figure 5. The volumes of these two boilers are 924 cm^3 and 221 cm^3, respectively. The ideal gas law and Wilson equation[13] are used for vapor-phase and liquid-phase fugacity calculations. The liquid holdups of these two boilers are found to be 1.25 cm^3 and 0.2 cm^3, respectively. When the larger boiler was used, half of the data were measured by adding approximately 0.7 to 51 g of n-heptane to 126 g of ethanol; the other half were measured by adding approximately 0.08 to 14 g of ethanol to 138 g of n-heptane. When the smaller boiler was used, half of the data were measured by adding approximately

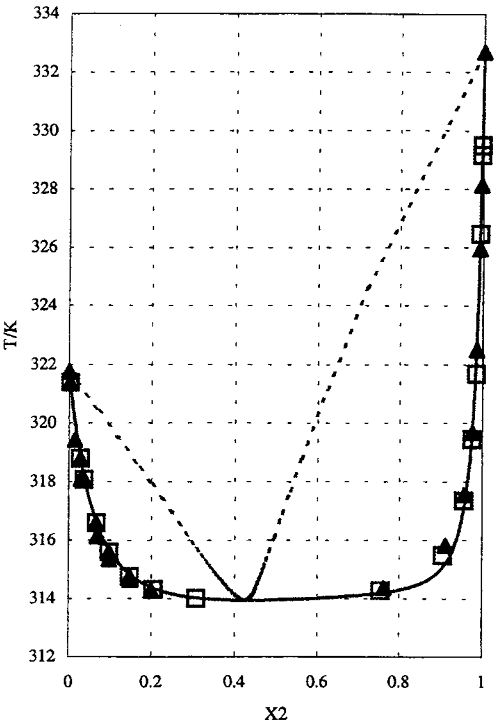

Figure 5. Vapor−liquid equilibrium pressures and phase compositions for ethanol (1) + *n*-heptane (2) at 27.58 kPa. The open squares and solid triangles denote temperatures measured by the 924 cm^3 boiler and the 221 cm^3 boiler, respectively. The solid and broken lines are the calculated liquid and vapor coexistence curves, respectively.

0.9 to 4.3 g of *n*-heptane to 27 g of ethanol; the other half were measured by adding approximately 0.05 to 2.5 g of ethanol to 25 g of *n*-heptane. The weights of added ethanol were measured to 0.0001 g except for the last three big adds when the larger boiler was used. All other weights were measured to 0.001 g.

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