Phase Equilibria for 1,1,1,2,3,4,4,5,5,5-Decafluoropentane + 2-Methylfuran, 2-Methylfuran + Oxolane, and 1,1,1,2,3,4,4,5,5,5-Decafluoropentane + 2-Methylfuran + Oxolane at 35 kPa

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Vapor−liquid equilibrium data at 35 kPa have been determined for the ternary system 1,1,1,2,3,4,4,5,5,5-decafluoropentane (HFC-4310mee) + 2-methylfuran + oxolane, and for their constituent binaries HFC-4310mee + 2-methylfuran and 2-methylfuran + oxolane, in the temperature range 297 to 310 K. Vapor pressures of 2-methylfuran have also been measured in the range of boiling temperatures of the mixture. Depending on the concentration range, the ternary system exhibits positive to negative deviations from ideal behavior and no ternary azeotrope has been detected. The binary system HFC-4310mee (1) + 2-methylfuran (2) exhibits positive deviations form ideal behavior and a minimum temperature azeotrope at a composition rich in HFC-4310mee ($x_1 \cong 0.561$, $T \cong 297.55$ K). The binary system 2-methylfuran (2) + oxolane (3) exhibits negative deviations form ideal behavior and a maximum temperature azeotrope at a composition rich in oxolane ($x_2 \cong 0.310$, $T \cong 309.95$ K). The vapor−liquid equilibrium data of the binary mixtures were correlated with the Redlich−Kister model and were used to predict the equilibrium properties of the ternary mixture. In addition, a model-free approach that is applicable to ternary mixtures has been used to analyze the properties of the ternary mixture.

Introduction

Azeotropic mixtures of decafluoropentane with many different compounds have been widely patented as solvents, aerosol propellants, heat transfer fluids, blowing agents, polymerization media, carrier fluids, gaseous dielectrics, and power cycle working fluids.[1] Despite their practical interest, experimental vapor−liquid equilibrium (VLE) data are scarce for these mixtures in the full concentration range. Moreover, the behavior of the fluorine functional group is important from a theoretical viewpoint because of its ability to form polyazeotropic binary mixtures. For example, Kao et al.[2] have reported polyazeotropic behavior for the binary system 1,1,1,2,3,4,4,5,5,5-decafluoropentane (HFC-4310mee) + oxolane (THF). Polyazeotropy has been also observed in the systems benzene + hexafluorobenzene[3,4] and ammonia + 1,1-difluoro,2,2,2-trifluoroethane.[5] Phase equilibrium data of polyazeotropic mixtures are important for establishing the evolution pattern of azeotropic behavior with temperature and to analyze the effect of the solvent. In addition, the experimental information available allows testing of theories and models for predicting complex azeotropic behavior in multicomponent mixtures.

Equilibrium boiling temperatures and liquid-phase mole fractions for the system HFC-4310mee + THF have been reported by Kao et al.[2] at 323.18 K and at 26.68 and 58.58 kPa. According to their data, two stationary points of the boiling temperature are present at 26.68 kPa, in the range of concentrated THF. The topology of this polyazeotropic system has been confirmed and described in detail by Loras et al.,[1] who reported VLE measurements at 23, 26.68, 35, 45, and 55 kPa. According to Loras et al., the polyazeotropy of the system HFC-4310mee + THF ends *in a tangent azeotrope* as the equilibrium pressure increases to about 42 kPa. VLE data for the binary system 2-methylfuran + THF at 101.3 kPa have been reported by Boldyrev et al.[6] According to their results, the system 2-methylfuran + THF exhibits slight negative deviations from ideal behavior and no azeotrope is present. No VLE data have been reported for the binary system HFC-4310mee + 2-methylfuran.

The present work was undertaken to measure complete VLE data for the title systems, for which no data exist or only inaccurate VLE data are available to describe the azeotropic behavior of the ternary mixture. The pressure (35 kPa) was selected by considering that the system HFC-4310mee + THF exhibits polyazeotropic behavior at this pressure.

Experimental Section

Chemicals. THF (99.9 mass %, anhydrous) and 2-methylfuran (99 mass %) were purchased from Aldrich, and HFC-4310mee (99.9 mass %) was donated by DuPont. The reagents were used without further purification after gas chromatography failed to show any significant impurities. The densities of pure liquids were measured at 298.15 K using an Anton Paar DMA 55 densimeter. Temperature was controlled to ±0.01 K with a thermostated bath. The accuracy in density measurements is ±0.01 kg·m^{-3}. The experimental values of these properties and the boiling

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Table 1. Mole % Purities (mass %) and Normal Boiling Points *T* of Pure Components

component	purity/ mass %	ρ/kg·m^{-3}		T/K	
		expt	lit.	expt	lit.
HFC-4310mee	99.9	1581.62[a]			
		1595.73[b]		326.85	
2-methylfuran	99.0	909.46[a]		337.1	337.03[e]
		915.40[b]	915.00[c]		
THF	99.9	882.09[a]	882.30[d]	339.0	339.08[f]
		887.53[b]	887.20[d]		

[a] Measured at 293.15 K. [b] Measured at 298.15 K. [c] Smith and La Bonte.[19] [d] Ramkumar and Kudchadker.[20] [e] Krevor and Prausnitz.[12] [f] Wu and Sandler.[21]

Table 2. Experimental Vapor−Liquid Equilibrium Data for the Binary System HFC-4310mee (1) + 2-Methylfuran (2) at 35.00 kPa

T/K	x_1	y_1	γ_1	γ_2
308.20	0.000	0.000		1.000
306.05	0.015	0.093	4.854	1.006
302.85	0.050	0.223	4.007	1.022
300.65	0.101	0.291	2.851	1.083
299.25	0.175	0.365	2.197	1.123
298.85	0.205	0.395	2.066	1.130
298.45	0.278	0.422	1.658	1.210
298.15	0.322	0.444	1.526	1.256
297.95	0.382	0.467	1.365	1.333
297.75	0.431	0.495	1.294	1.383
297.65	0.483	0.520	1.219	1.454
297.55	0.537	0.549	1.163	1.532
297.55	0.590	0.578	1.114	1.619
297.65	0.646	0.614	1.076	1.707
297.75	0.694	0.646	1.049	1.803
297.95	0.743	0.683	1.027	1.906
298.15	0.803	0.740	1.020	2.021
298.55	0.855	0.800	1.017	2.076
298.95	0.894	0.849	1.014	2.106
299.45	0.945	0.909	1.004	2.394
300.42	1.000	1.000	1.000	

Table 3. Experimental Vapor−Liquid Equilibrium Data for the Binary System 2-Methylfuran (2) + THF (3) at 35.00 kPa

T/K	x_2	y_2	γ_2	γ_3
309.65	0.000	0.000		1.000
309.75	0.054	0.048	0.835	1.002
309.85	0.110	0.101	0.859	1.002
309.85	0.156	0.147	0.881	1.003
309.95	0.205	0.198	0.900	0.997
309.95	0.253	0.249	0.917	0.993
309.95	0.301	0.300	0.928	0.989
309.95	0.347	0.351	0.942	0.982
309.85	0.399	0.406	0.952	0.980
309.85	0.447	0.460	0.962	0.969
309.75	0.498	0.516	0.973	0.960
309.65	0.545	0.568	0.983	0.949
309.55	0.594	0.620	0.988	0.940
309.45	0.640	0.669	0.994	0.927
309.35	0.687	0.717	0.996	0.915
309.15	0.751	0.780	0.999	0.902
308.95	0.804	0.831	1.003	0.887
308.75	0.852	0.875	1.004	0.876
308.55	0.902	0.920	1.006	0.854
308.35	0.953	0.962	1.003	0.852
308.25	0.981	0.985	1.002	0.836
308.20	1.000	1.000	1.000	

Table 4. Experimental Vapor−Liquid Equilibrium Data for the Ternary System HFC-4310mee (1) + 2-Methylfuran (2) + THF (3) at 35.00 kPa

T/K	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3
298.55	0.504	0.427	0.535	0.438	1.154	1.543	0.626
298.75	0.704	0.231	0.683	0.297	1.045	1.921	0.473
299.05	0.276	0.667	0.415	0.563	1.597	1.242	0.609
299.35	0.389	0.502	0.467	0.489	1.260	1.414	0.622
299.35	0.595	0.289	0.609	0.335	1.072	1.688	0.740
300.25	0.889	0.059	0.889	0.092	1.008	2.164	0.539
300.45	0.795	0.108	0.800	0.163	1.005	2.091	0.557
300.95	0.187	0.701	0.330	0.611	1.719	1.181	0.763
301.05	0.393	0.405	0.453	0.438	1.121	1.457	0.774
301.35	0.521	0.264	0.567	0.333	1.045	1.681	0.657
301.85	0.315	0.458	0.410	0.475	1.221	1.353	0.700
302.25	0.694	0.095	0.751	0.152	0.999	2.046	0.623
302.55	0.190	0.605	0.321	0.565	1.537	1.182	0.748
302.65	0.088	0.806	0.257	0.683	2.648	1.068	0.754
302.95	0.389	0.311	0.446	0.364	1.026	1.458	0.835
303.35	0.502	0.192	0.564	0.268	0.987	1.711	0.712
303.65	0.320	0.352	0.400	0.405	1.084	1.390	0.762
303.85	0.097	0.710	0.231	0.640	2.060	1.080	0.843
304.15	0.189	0.504	0.304	0.506	1.365	1.187	0.778
304.75	0.396	0.213	0.465	0.288	0.972	1.559	0.772
304.95	0.306	0.293	0.388	0.345	1.040	1.347	0.809
304.95	0.601	0.060	0.690	0.099	0.942	1.873	0.755
305.35	0.095	0.607	0.204	0.587	1.730	1.087	0.839
305.35	0.496	0.110	0.569	0.174	0.925	1.775	0.779
305.45	0.190	0.407	0.275	0.438	1.167	1.206	0.843
306.15	0.045	0.717	0.127	0.690	2.191	1.047	0.888
306.15	0.233	0.303	0.313	0.347	1.047	1.246	0.846
306.55	0.124	0.442	0.204	0.459	1.265	1.111	0.880
306.55	0.292	0.213	0.341	0.277	0.897	1.394	0.874
307.35	0.151	0.317	0.214	0.349	1.050	1.142	0.901
307.85	0.048	0.519	0.104	0.524	1.577	1.025	0.923
307.85	0.405	0.062	0.460	0.100	0.824	1.631	0.889
308.05	0.294	0.115	0.329	0.160	0.805	1.394	0.924
308.15	0.164	0.204	0.202	0.236	0.880	1.158	0.946
308.35	0.202	0.161	0.233	0.197	0.823	1.215	0.942
308.85	0.099	0.202	0.130	0.215	0.908	1.037	0.969
309.05	0.049	0.311	0.084	0.317	1.177	0.985	0.959
309.05	0.106	0.097	0.119	0.103	0.779	1.027	0.999
309.05	0.198	0.071	0.209	0.088	0.729	1.203	0.985
309.35	0.057	0.050	0.063	0.048	0.758	0.922	1.007

points are given in Table 1 together with those given in the literature, when available.

Apparatus and Procedure. An all-glass Fischer LABODEST vapor−liquid equilibrium apparatus model 602/D, manufactured by Fischer Labor und Verfahrenstechnik (Germany), was used in the equilibrium determinations. The equilibrium vessel was a dynamic recirculating still, equipped with a Cottrell circulation pump. The still is capable of handling pressures from 0.25 to 400 kPa and temperatures up to 523 K. The Cottrell pump ensures that both liquid and vapor phases are in intimate contact during boiling and also in contact with the temperature sensing element. The equilibrium temperature was measured with a digital Fischer thermometer with an accuracy of ±0.1 K. The apparatus is equipped with two digital pressure sensors: one for the low-pressure region, with an accuracy of ±0.01 kPa, and another for the high-pressure region, with an accuracy of ±0.1 kPa. The temperature probe was calibrated against the ice and steam points of distilled water. The manometers were calibrated by using the vapor pressure of ultrapure water. The still was operated under constant pressure until equilibrium was reached. Equilibrium conditions were assumed when constant temperature and pressure were observed for 30 min or longer. Then, samples of liquid and condensate were taken for analysis. The sample extractions were carried out with special syringes that allowed withdrawal of small volume samples (0.1 mL) in a system under partial vacuum conditions.

Analysis. The concentrations of the liquid and condensed phases were determined using a CE Instruments GC 8000 Top gas chromatograph (GC), after calibration with gravimetrically prepared standard solutions. A flame ionization detector was used together with a 30 m, 0.454

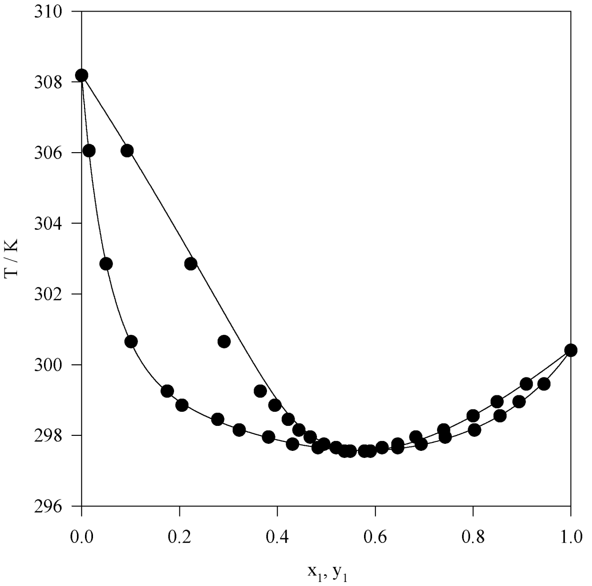

Figure 1. Experimental data for the system HFC-4310mee (1) + 2-methylfuran (2) at 35.00 kPa: (●) experimental data reported in this work; (—) data smoothed with the Legendre polynomial used in point-to-point consistency analysis.

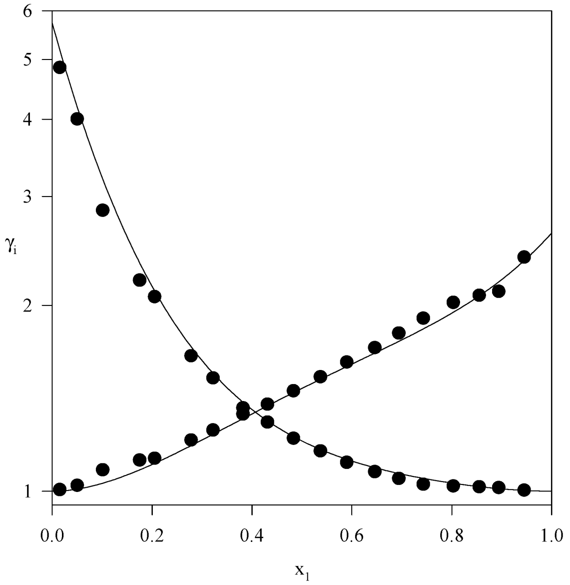

Figure 2. Activity coefficient plot of the system HFC-4310mee (1) + 2-methylfuran (2) at 35.00 kPa: (●) experimental data reported in this work; (—) data smoothed with the Legendre polynomial used in point-to-point consistency analysis.

mm i.d., capillary column DB-MTBE (J & W Scientific). The GC response peaks were treated with Chrom-Card for Windows, version 1.21. The column, injector, and detector temperatures were (373, 498, and 523) K, respectively. Very good peak separation was achieved under these conditions, and calibration analyses were carried out to convert the peak area ratio to the mass composition of the sample. The standard deviation for reported measurements in the mole fraction was usually less than 0.001.

Results

The temperature T and liquid-phase x and vapor-phase y mole fraction measurements at $P = 35.00$ kPa are reported in Tables 2−4 and are shown in Figures 1−4. The tables and figures also report the activity coefficients γ_i that

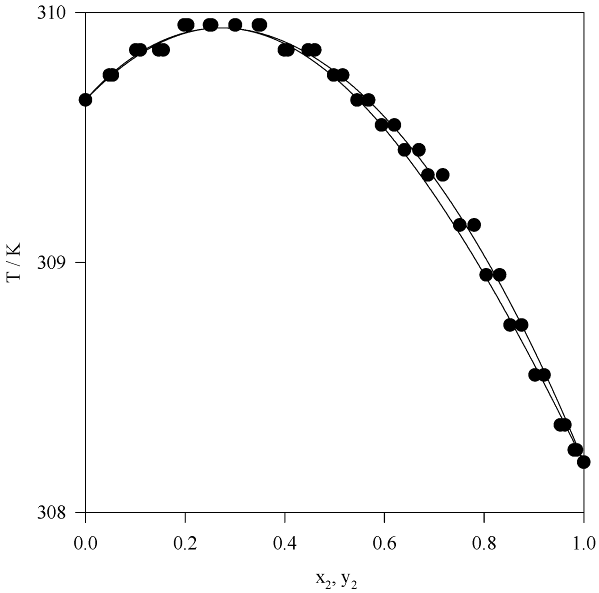

Figure 3. Experimental data for the system 2-methylfuran (2) + THF (3) at 35.00 kPa: (●) experimental data reported in this work; (—) data smoothed with the Legendre polynomial used in point-to-point consistency analysis.

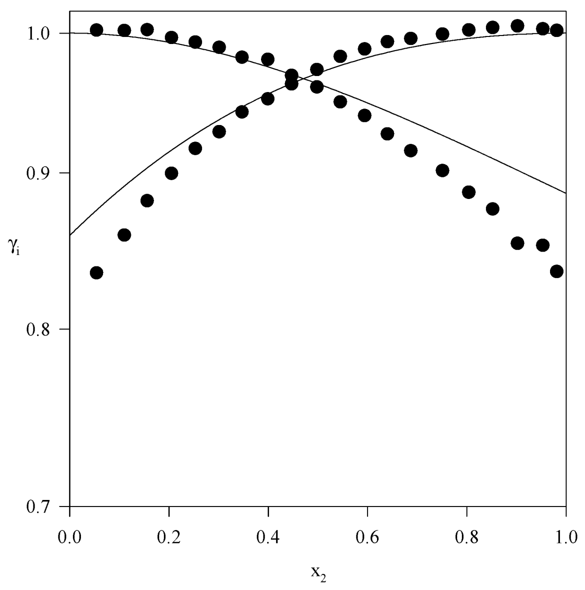

Figure 4. Activity coefficient plot of the system 2-methylfuran (2) + THF (3) at 35.00 kPa: (●) experimental data reported in this work; (—) data smoothed with the Legendre polynomial used in point-to-point consistency analysis.

were calculated from the following equation,[7]

$$\gamma_i = \frac{y_i P}{x_i P_i^\circ} \tag{1}$$

where P is the total pressure and P_i° is the pure component vapor pressure. In eq 1, the vapor phase is assumed to be an ideal gas and the pressure dependence of the liquid-phase fugacity is neglected. Equation 1 was selected to calculate activity coefficients because, at the low pressures observed in the present VLE data, these simplifications are reasonable. In addition, scarce physical information is available for HFC-4310mee, so that an accurate estimation of the second virial coefficients of this component and their mixtures is not possible. However, according to the data of Tripp and Dunlap[8] for decafluorobutane and of Garner

Table 5. Experimental Vapor Pressure Data for 2-Methylfuran

T/K	$P°$/kPa	T/K	$P°$/kPa	T/K	$P°$/kPa
289.05	15.03	321.85	59.44	329.05	77.10
295.25	20.09	316.55	48.77	330.25	80.31
300.25	25.05	319.05	53.55	332.15	85.89
304.05	29.52	321.85	59.44	333.95	91.11
309.05	36.27	323.95	64.26	335.35	95.74
319.05	53.55	326.65	70.91	336.85	100.53

Table 6. Antoine Coefficients, Eq 2

compound	A_i	B_i	C_i
HFC-4310mee [a]	6.438 76	1242.510	46.568
2-methylfuran[b]	6.285 28	1268.031	40.752
THF[a]	6.148 52	1211.079	46.627

[a] Parameters taken from Loras et al. [b]Calculated from the vapor pressure data presented in Table 5.

and McCoubrey[9] for dodecafluoropentane, it is possible to estimate that the order of magnitude of the second virial coefficient of HFC-4310mee is -1000 cm^3·mol^{-1} at 300 K. Similar values have been reported by Hossenlopp and Scott[10] for THF and by Eon et al.[11] for 2-methylfuran. From these values it follows that the maximum error related to the approximation of the vapor-phase fugacity by means of ideal gas relations is on the order of 2% for the present data.

The pure component vapor pressures $P_i°$ for 2-methylfuran were determined experimentally as a function of the temperature using the same equipment as that for obtaining the VLE data; the pertinent results are presented in Table 5. The measured vapor pressures were correlated using the Antoine equation,

$$\log(P_i°/\text{kPa}) = A_i - \frac{B_i}{(T/\text{K}) - C_i} \qquad (2)$$

where the constants A_i, B_i, and C_i are reported in Table 6. The experimental vapor pressures of 2-methylfuran were correlated with an average percentage deviation [MADP] of 0.1%. In addition, the parameters presented in Table 6 successfully predict the experimental vapor pressures reported by Krevor and Prausnitz[12] for 2-methylfuran [MADP = 0.6%], as shown in Figure 5. The parameters of eq 2 for HFC-4310mee and THF have been taken from the work of Loras et al.[1] The calculated activity coefficients reported in Tables 2−4 are estimated to be accurate to within ±3%. The results reported in Table 2 indicate that the system HFC-4310mee (1) + 2-methylfurane (2) deviates positively from ideal behavior and exhibits a single azeotrope (Figure 1). According to Table 3 and Figure 3, the system 2-methylfurane (2) + THF (3) deviates negatively from ideal behavior and also presents a single azeotropic point. The azeotropic concentrations of the measured binaries were estimated by fitting the function

$$f(x) = 100\frac{y - x}{x} \qquad (3)$$

where *f(x)* is an empirical interpolating function and *x* and *y* have been taken from the experimental data. Azeotropic concentrations, as determined by solving $f(x) = 0$, are indicated in Table 7.

The VLE data for binaries reported in Tables 2 and 3 were found to be thermodynamically consistent by the point-to-point method of Van Ness et al.,[13] as modified by Fredenslund et al.[14] ($\Delta y < 0.01$). Pertinent consistency statistics and details are presented in Table 8.

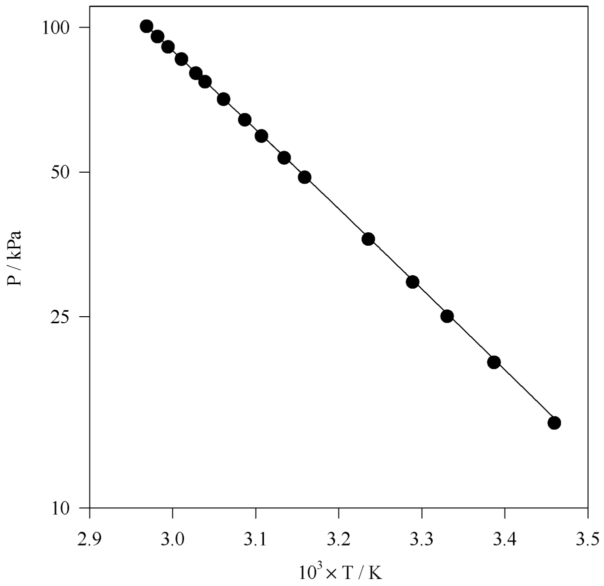

Figure 5. Comparison of correlated vapor pressures for 2-methylfuran with other references: (●) experimental data reported by Krevor and Prausnitz;[12] (—) data predicted by eq 2 and the parameters given in Table 6.

Table 7. Estimated Azeotropic Coordinates for the Binary Systems

system	$x^{\text{Az}\,(a)}$	T^{Az}/K
HFC-4310mee (1) + 2-methylfuran (2)	0.561	297.55
2-methylfuran (2) + THF (3)	0.310	309.95

[a] Referred to the first component of the binary mixture.

Table 8. Consistency Test Statistics for the Binary Systems Reported in This Work

system	N_p[a]	$100\Delta y$[b]	ΔP[c]/kPa
HFC-4310mee (1) + 2-methylfuran (2)	3	0.9	0.05
2-methylfuran (2) + THF (3)	2	0.3	0.03

[a] Number of parameters for the Legendre polynomial. [b] Average absolute deviation in vapor-phase mole fractions $\Delta y = 1/N\Sigma_{i=1}^{N} |y_1^{\text{expt}} - y_1^{\text{calc}}|$ (N = number of data points). [c] Average absolute deviation in pressure $\Delta P = 1/N\Sigma_{i=1}^{N}|P^{\text{expt}} - P^{\text{calc}}|$.

The binary VLE data presented in Tables 2 and 3, together with the data reported by Loras et al.[1] for the system HFC-4310mee (1) + THF (3) at 35 kPa, were correlated using the Redlich−Kister expansion[15]

$$\frac{G^{\text{E}}}{RT} = x_i x_j[C_1^{ij} + C_2^{ij}(x_j - x_i) + C_3^{ij}(x_j - x_i)^2] \qquad i \neq j \quad (4)$$

where C_k^{ij} are the constants for the pertinent *ij* binary, assumed to be independent of the temprature. The following objective function (OF) has been used for fitting purposes,

$$\text{OF} = \sum_{i=1}^{N}(|P_i^{\text{expt}} - P_i^{\text{calc}}|/P_i^{\text{expt}} + |y_i^{\text{expt}} - y_i^{\text{calc}}|)^2 \qquad (5)$$

and pertinent parameters are reported in Table 9, together with the relative deviation of the vapor pressures and the vapor-phase mole fraction. No other standard excess Gibbs energy (G^{E}) model, such as NRTL, UNIQUAC, and Wilson (Walas[16]), was considered here because it has been pointed

Table 9. Constants for the Redlich−Kister Model and Fit, Correlation, and Prediction Statistics

A. Parameters Fitted from Binary Data

system	C_1^{ij}	C_2^{ij}	C_3^{ij}
HFC-4310mee (1) + 2-methylfuran (2)[a]	1.1346	−0.4022	0.1977
HFC-4310mee (1) + THF (3)[b]	−0.6260	−0.1038	0.2880
2-methylfuran (2) + THF (3)[a]	−0.1555	0.0279	0.0410

B. Parameters Fitted from Ternary Data

D_0	D_1	D_2
0.2089	−0.2911	0.1129

C. VLE Correlations and Predictions

	bubble-point pressures			dew-point pressures		
system	ΔP^c/%	$100\Delta y_1{}^d$	$100\Delta y_2$	ΔP/%	$100\Delta x_1$	$100\Delta x_2$
1 + 2[a]	0.20	0.9	0.9	0.68	1.2	1.2
1 + 3[b]	0.29	0.5		0.36	0.5	
2 + 3[a]	0.23		0.2	0.24		0.2
1 + 2 + 3[e]	0.63	0.6	0.4	0.99	0.6	0.5
1 + 2+3[f]	0.36	0.6	0.4	0.77	0.6	0.5

[a] Calculated from the data for binaries reported in this work. [b] Calculated from the data of Loras et al.[1] [c] Average percentage deviation in pressure $\Delta P = 100/N\Sigma_i^N |P_i^{\text{expt}} - P_i^{\text{calc}}|/P_i^{\text{expt}}$. [d] Average absolute deviation in mole fraction $\Delta y = 1/N\Sigma_i^N |y_i^{\text{expt}} - y_i^{\text{calc}}|$. [e] Prediction from binary parameters ($D_0 = D_1 = D_2 = 0$). [f] Prediction using ternary parameters.

Table 10. Parameters and Correlation Statistics for the Bubble Temperatures of the System HFC-4310mee (1) + 2-Methylfuran (2) + THF (3) at 35.00 kPa

Binary Parameters for Eq 8

	binary system		
parameter	1 + 2	1 + 3	2 + 3
A_{ij}	−1.151752	0.548270	0.134781
B_{ij}	0.515338	−0.200738	−0.020873
C_{ij}	−0.675389	−0.387791	−0.013308
D_{ij}	0.544803	0.237984	
E_{ij}	−0.991907		
F_{ij}	1.096887		
G_{ij}	0.753716		
H_{ij}	−1.034611		
I_{ij}	−1.719579		
J_{ij}	1.635115		
ΔT^a/K	0.05	0.06	0.02
$\sigma_T{}^b$/K	0.06	0.08	0.02

Ternary Parameters for Eq 8

Q_0	0.225642	Q_{22}	−0.719705
Q_{11}	−2.238063	Q_{23}	−0.465920
Q_{12}	−1.823708	Q_{31}	5.320497
Q_{21}	−2.262001		
ΔT^a/K	0.06		
$\sigma_T{}^b$/K	0.08		

Additional Constants Needed in Eq 7

component	$\Delta H_i{}^{\circ\,c}$/J·mol^{-1}	$T_i{}^\circ$/K
1	33314	300.42
2	32236	308.20
3	32133	309.65

[a] Average absolute deviation in temperature $\Delta T = 1/N\Sigma_{i=1}^N|T_i^{\text{expt}} - T_i^{\text{calc}}|$. [b] Standard deviation. [c] Enthalpy of vaporization and bubble temperatures calculated from the Antoine equation at the pressure of the system.

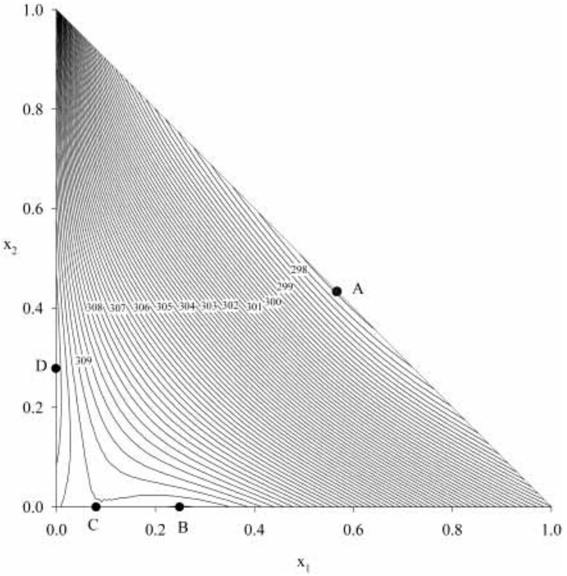

Figure 6. Isotherms for the ternary system HFC-4310mee (1) + 2-methylfuran (2) + THF (3) at 35.00 kPa: (—) smoothed with eq 7 and the coefficients given in Table 10; (●) azeotropic points.

out by Loras et al.[1] that G^E models have a limited ability to interpolate the polyazeotropic data of the system HFC-4310mee (1) + THF (3). The binary parameters were then used to fit the VLE data of the ternary system using the Redlich−Kister expansion

$$\frac{G^E}{RT} = \sum_{j>i}^{3} x_i x_j [C_1^{ij} + C_2^{ij}(x_j - x_i) + C_3^{ij}(x_j - x_i)^2] + x_1 x_2 x_3 [D_0 + D_1 x_1 + D_2 x_2] \quad (6)$$

where D_0, D_1, and D_2 are ternary constants. After smoothing the data with eq 6, using the objetive function of eq 5, the ternary constants were found to be statistically significant, suggesting that the ternary data cannot be predicted accurately from the binary contributions. Prediction and correlation results are presented in Table 9. The statistics shown in the table indicate a fair prediction of the equilibrium pressures and concentrations when using binary contributions (case in which $D_0 = D_1 = D_2 = 0$), a fact that suggests consistency of the experimental ternary data. However, the correlation of the data improves when using the ternary parameter. In addition, no azeotrope is predicted by eq 6 and the parameters given in Table 9 for the ternary mixture.

Since the ternary system presented in this work is difficult to model using conventional approaches for multicomponent systems, the alternative model-free technique proposed recently by Lam et al.[17,18] was used to analyze its reliability and excess properties. In the approach by Lam et al., applied to isobaric systems, it is assumed that the pressure is constant and equal to the experimental value (35 kPa). In addition, the approach requires fitting of the boiling point temperatures using a flexible smoothing function of the liquid-phase mole fractions. The following expression has been used for this purpose[18]

$$T = \frac{\sum_{i=1}^{3} x_i \Delta\tilde{H}_i{}^\circ/R}{\sum_{i=1}^{3} x_i \Delta\tilde{H}_i{}^\circ/RT_i{}^\circ - \Omega} \quad (7)$$

In eq 7, $\Delta\tilde{H}_i{}^\circ$ is the enthalpy of vaporization of pure components, $T_i{}^\circ$ is their respective boiling temperature at the pressure of the system, and R is the gas constant. In

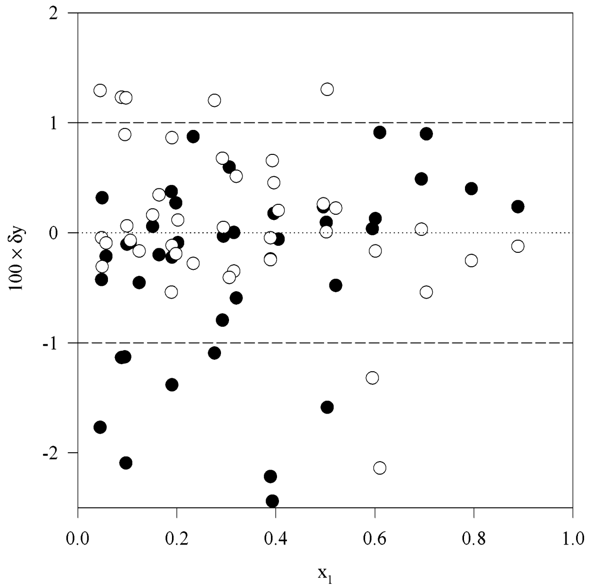

Figure 7. Vapor-phase mole fraction residuals for the ternary system HFC-4310mee (1) + 2-methylfuran (2) + THF (3) at 35.00 kPa, as calculated from the model-free approach: (●) δy_1; (○) δy_2; ($\delta y_k = y_k^{\text{cal}} - y_k^{\text{exptl}}$).

addition, Ω corresponds to the following empirical function of the Redlich−Kister type

$$\Omega = \sum_{j>i}^{3} x_i x_j (A_{ij} + B_{ij}\{x_i - x_j\} + C_{ij}\{x_i - x_j\}^2 + ...) + x_1 x_2 x_3 (Q_0 + x_1 Q_{11} + x_2 Q_{12} + \sum_{k\geq 2}[Q_{k1}\{x_1 - x_2\}^k + Q_{k2}\{x_1 - x_3\}^k + Q_{k3}\{x_2 - x_3\}^k]) \quad (8)$$

where A_{ij}, B_{ij}, C_{ij}, ... are binary parameters and Q_0, Q_{ij} are ternary parameters. As indicated in ref 18, eq 7 is able to fit simultaneously the bubble temperatures of the ternary system and its constituent binaries, within the range of experimental errors for $T-x$ determinations. In addition, for mixtures that exhibit positive deviation azeotropes, it is necessary to provide fitting constraints to avoid nonphysical results in excess properties.[18] Table 10 reports the various constants of eqs 7 and 8, together with the fitting statistics. Figure 6 displays the map of isotherms obtained from eq 7, from which it is deduced that, although each constituent binary is azeotropic (see points A, B, C, and D in Figure 6), no azeotrope is present for the ternary mixture. The former result is in good agreement with the prediction of the Redlich−Kister model and the trend observed in the present VLE data.

Equation 7 has been used for calculating numerically the G^E function and vapor-phase mole fractions of the ternary mixture as explained in ref 17. After a satisfactory $T-x$ fit has been performed, and provided that data of enthalpys of mixing (ΔH) are available, the model-free approach is able to calculate properties of isobaric systems by integrating the Gibbs−Duhem equation. No experimental ΔH data are available for mixtures that contain HFC-4310mee, and for this reason, it has been assumed that the isobaric ternary mixture is regular, that is,

$$G^E = \Delta H \quad (9)$$

Figure 7 shows the residuals calculated using the vapor-phase mole fractions predicted by the model-free approach, as calculated assuming regular behavior for the liquid phase and ideal gas behavior for the vapor phase. The overall deviations satisfy the consistency criteria proposed by Fredenslund et al.[14] (Δy_1 = 0.006, Δy_2 = 0.005). However, as shown in Figure 7, although residuals are randomly scattered, they are biased toward a slight underprediction of the vapor-phase concentration. This behavior may be attributed mainly to the assumption of regularity in eq 9.

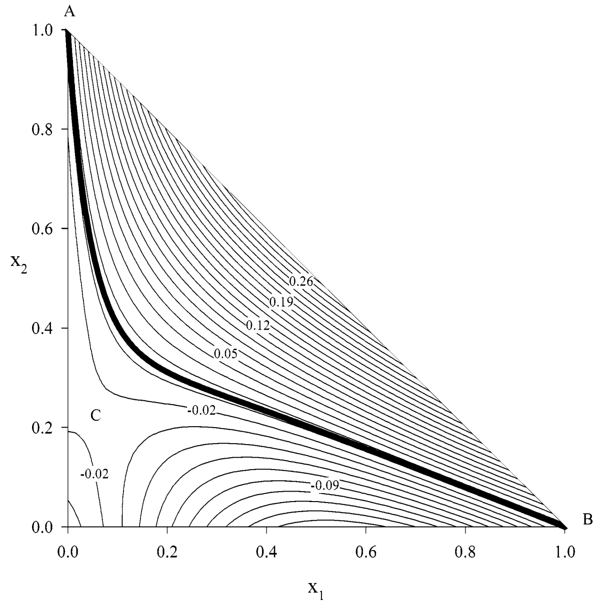

Figure 8. Excess Gibbs energy function for the ternary system HFC-4310mee (1) + 2-methylfuran (2) + THF (3) at 35.00 kPa: (—) calculated from a model-free approach from eq 7 and the coefficients given in Table 10. The bold line is the line of zero excess energy.

The calculated G^E function is presented in Figure 8, from which it can be concluded that the ternary system exhibits mixed deviations from ideal behavior. Center curve A−B corresponds to the value $G^E = 0$. The region located at the right-hand side of A−B is characterized by positive deviations, consistent with the experimental data for the system HFC-4310mee (1) + 2-methylfuran (2). In contrast, the region located at the left-hand side of A−B is characterized by negative deviations from ideality, which corresponds to the behavior observed for the binary system 2-methylfuran (2) + THF (3). The negative deviation region includes the saddle point C for the G^E function of the ternary system; its influence is observed on the inflectant behavior of the excess function of the binary system HFC-4310mee (1) + THF (3),[1] as required for polyazeotopy.

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