Isothermal Vapor−Liquid Equilibrium Data for the Hexafluoropropylene (R1216) + Propylene System at Temperatures from (263.17 to 353.14) K

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Isothermal vapor−liquid equilibrium (VLE) data are presented for the system hexafluoropropylene (R1216) + propylene (R1270). Measurements were performed for six isotherms ranging from (263.17 to 353.14) K, at pressures from (0.224 to 4) MPa. The measurements were undertaken using a "static−analytic" type apparatus, with sampling of the equilibrium phases via pneumatic capillary samplers (Rolsi, Armine's patent). The apparatus and the samplers were developed in the CEP/TEP laboratory. The uncertainties in the measurements are within ± 0.02 K, ± 0.0005 MPa, and less than ± 4.0 % for temperature, pressure, and mole fractions, respectively. The full set of isothermal VLE data is correlated with the Peng−Robinson equation of state (PR EoS), incorporating the original Soave α function, with the Wong−Sandler mixing rule utilizing the nonrandom two-liquid (NRTL) activity coefficient model.

Introduction

Fluoropropylenes are good candidates within the next generation of refrigerants which can satisfy both the Montreal and the Kyoto Protocols. They have no chlorine atoms and consequently are safe for the ozone layer, and their global warming potentials (GWP) are lower than 1 (Acerboni et al.[1]). Considering a time horizon of 20 years, the GWP of hexafluoropropylene (R1216) is 0.86 (1 for CO_2). It is also indicated that the lifetime of C_3F_6 is 6 days. Clodic,[2] in 2008, has mentioned that fluoropropylenes (like R1234yf) are interesting fluids which can conveniently replace R134a without major modifications to existing refrigeration systems.

As these refrigerants may prove to be good candidates as possible replacements, the refrigeration industry needs experimental data concerning R1216 and its mixtures with other compounds to optimize process efficiencies. Moreover, as mentioned in a previous paper (Ramjugernath et al.[3]), "refrigerant" compounds can be used as "solvent" compounds for separation processes. The new generated data will also enable the improvement of the predictive Soave−Redlich−Kwong (PSRK) equation of state by optimization of interaction parameters for certain functional groups.

Therefore, vapor−liquid equilibrium (VLE) measurements were undertaken at six temperatures for hexafluoropropylene + propylene. After careful examination of the open literature, it seems that this system has not previously been studied, and the measurements herein represent new data.

The experimental VLE data have been correlated with the Peng−Robinson[4] equation of state (PR EoS), incorporating the Soave α function, with the Wong−Sandler[5] (WS) mixing rule utilizing the nonrandom two-liquid (NRTL)[6] activity coefficient model. The correlated model parameters are presented. This system corresponds to type I according to the classification of van Konynenburg and Scott[7] and presents an azeotropic behavior.

Table 1. Critical Parameters and Acentric Factor[11]

compound	T_c / K	P_c / MPa	ω
R1216[a]	358.93	3.136	0.3529
R1270	365	4.620	0.148

[a] From Coquelet et al., ref 12.

Experimental Section

Materials. R1216 was provided by Pelchem and has a certified volume fraction purity of greater than 0.995. R1270 was obtained from l'Air Liquide and has a certified minimum volume fraction purity of 0.995. Both chemicals were used without any further purification. Their corresponding critical properties and parameters used in the data correlation are listed in Table 1.

Experimental Apparatus. The apparatus used for the VLE measurements in this work is based on a "static−analytic" method with sampling of both the liquid and the vapor phases. The apparatus is similar to that described by Laugier and Richon[8] and identical to that described by Ramjugernath et al.[3] The same experimental procedure is used.

Pt-100 probes were used to determine the temperature of the equilibrium cell. They were calibrated against a 25 Ω reference probe (TINSLEY precision instrument) certified by the Laboratoire National d'Essais (Paris) following the International Temperature Scale 1990 Protocol.

Pressures were measured using a pressure transducer (Druck, type PTX 611, range: 0 to 4 MPa). This sensor was calibrated against a dead weight pressure balance (model 5202S supplied by Desgranges and Huot).

Pressure and temperature data are recorded via a computer linked to an HP data acquisition unit (HP34970A). The resulting

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uncertainties in temperature and pressure are ± 0.02 K and ± 0.0005 MPa, respectively.

Analysis of samples of the equilibrium phases are performed using a gas chromatograph (VARIAN model CP-3800) equipped with a thermal conductivity detector (TCD) connected to a data acquisition system (WINILAB from Perichrom). The analytical column convenient for the separation of the studied system is the Haysep P model with 60/80 mesh (1/8" Silcosteel tube, 2.5 m length) supplied by Restek, France. A TCD was calibrated repeatedly by injections of known amounts of each pure component into the injector of the gas chromatograph using a gas-tight syringe. Taking into account the uncertainties due to calibrations and the deviations of analyses, the resulting uncertainties in vapor and liquid mole fractions are estimated to be less than ± 4.0 %.

For each equilibrium condition, at least five samples of both the vapor and the liquid phases are withdrawn using the ROLSI pneumatic samplers[9] (www.rolsi.com) and analyzed to check for repeatability of the measurements.

Correlations. The experimental VLE data are correlated using Thermosoft, in-house software developed by Armines/MINES-Paristech. The PR EoS[4] incorporating the Soave α function was selected for these purposes and together with the WS[5] mixing rule was used utilizing the NRTL activity coefficient model.[6]

$$b = \frac{\sum_i \sum_j x_i x_j \left(b - \frac{a}{RT}\right)_{ij}}{1 - \left(\frac{\sum_i x_i \frac{a_i}{b_i}}{RT} + \frac{g^{E}(T, P = \infty, x_i)}{CRT}\right)} \tag{1}$$

$$b - \frac{a}{RT} = \sum_i \sum_j x_i x_j \left(b - \frac{a}{RT}\right)_{ij} \tag{2}$$

$$\left(b - \frac{a}{RT}\right)_{ij} = \frac{1}{2}\left[\left(b - \frac{a}{RT}\right)_i + \left(b - \frac{a}{RT}\right)_j\right](1 - k_{ij}) \tag{3}$$

k_{ij} is an adjustable binary interaction parameter.

The excess Gibbs energy model chosen is the NRTL local composition model.

$$\frac{g^{E}(T, P, x_i)}{RT} = \sum_i x_i \sum_j \frac{x_j \exp\left(-\alpha_{ji}\frac{\tau_{ji}}{RT}\right)}{\sum_k x_k \exp\left(-\alpha_{ki}\frac{\tau_{ki}}{RT}\right)} \tau_{ji} \tag{4}$$

$\tau_{ii} = 0$ and $\alpha_{ii} = 0$.

α_{ji}, τ_{ji}, and τ_{ij} are adjustable parameters. It is recommended[6] to use $\alpha_{ji} = 0.3$ for systems like this one. τ_{ji} and τ_{ij} are adjusted directly to fit the experimental VLE data through a modified Simplex algorithm using the following objective function:

$$F = \frac{100}{N}\left[\sum_{1}^{N}\left(\frac{x_{\text{exp}} - x_{\text{cal}}}{x_{\text{exp}}}\right)^2 + \sum_{1}^{N}\left(\frac{y_{\text{exp}} - y_{\text{cal}}}{y_{\text{exp}}}\right)^2\right] \tag{5}$$

where N is the number of data points and x_{exp} and x_{cal} are the measured and calculated liquid-phase mole fractions, respectively.

Discussion

The experimental VLE data are presented in Tables 2 and 3. The parameters for the PR EoS with WS mixing rules incorporating the NRTL activity coefficient model are presented in Table 4. The measured experimental data are presented in Figure 1 with their representation through the selected model.

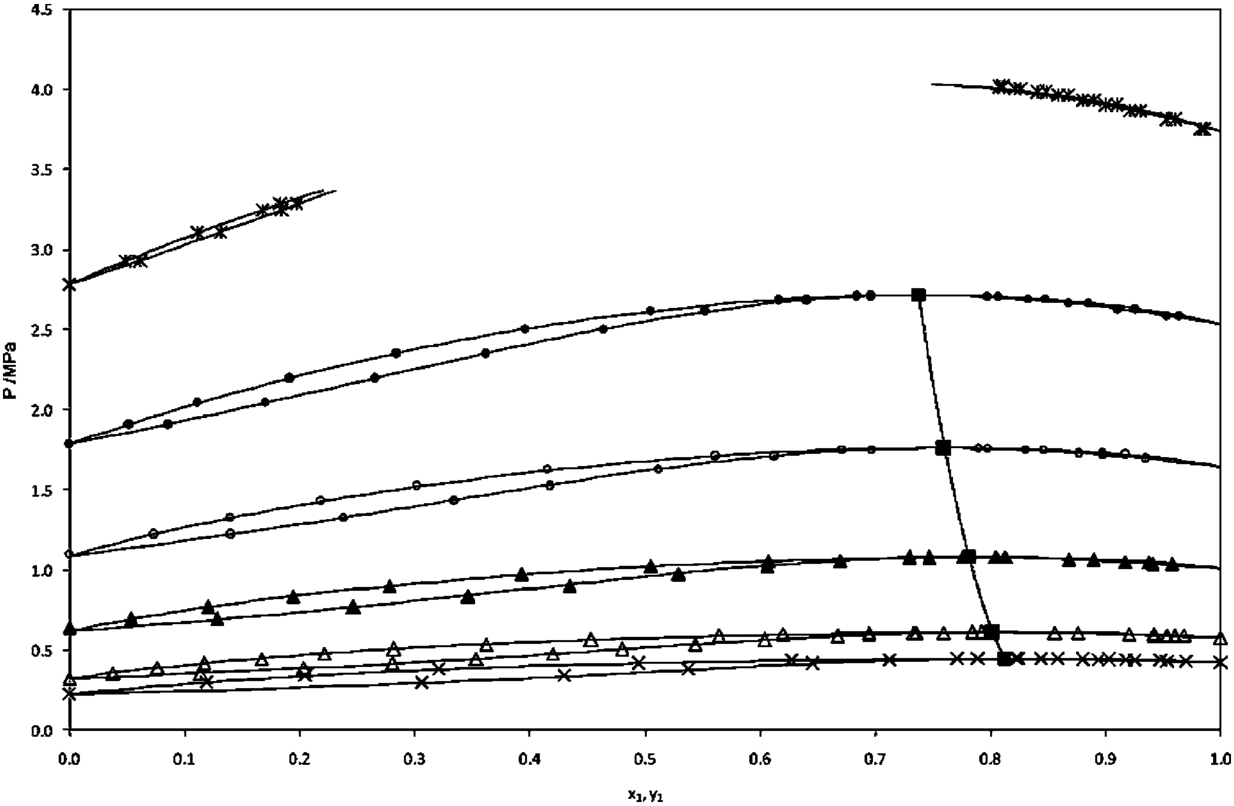

Figure 1. Plot of the $P-x-y$ data for the system R1270 (1) + R1216 (2): ×, 263.17 K; △, 273.16 K; ▲, 293.12 K; ○, 313.11 K; ●, 333.11 K; ∗, 353.14 K; —, model; ■, azeotrope location.

Table 2. *P*−*x*−*y* Data for the R1270 (1) + R1216 (2) System at (263.17, 273.16, and 293.12) K

T = 263.17 K			T = 273.16 K			T = 293.12 K		
P/MPa	x_1	y_1	P/MPa	x_1	y_1	P/MPa	x_1	y_1
0.2245	0	0	0.3244	0	0	0.6410	0	0
0.2977	0.119	0.306	0.3574	0.038	0.114	0.6946	0.053	0.128
0.3380	0.205	0.430	0.3878	0.077	0.204	0.7689	0.120	0.247
0.3780	0.321	0.538	0.4167	0.117	0.280	0.8390	0.194	0.347
0.4171	0.494	0.645	0.4479	0.166	0.353	0.9044	0.278	0.434
0.4348	0.628	0.712	0.4778	0.221	0.420	0.9746	0.392	0.529
0.4440	0.771	0.789	0.5064	0.282	0.480	1.0240	0.505	0.606
0.4447	0.822	0.824	0.5371	0.362	0.543	1.0554	0.607	0.670
0.4440	0.859	0.844	0.5647	0.453	0.603	1.0777	0.729	0.747
0.4410	0.903	0.880	0.5893	0.564	0.667	1.0800	0.776	0.7780
0.4392	0.918	0.894	0.5979	0.620	0.694	1.0798	0.813	0.805
0.4347	0.948	0.926	0.6068	0.694	0.735	1.0667	0.889	0.868
0.4296	0.970	0.954	0.6091	0.733	0.759	1.0514	0.937	0.916
			0.6117	0.784	0.791	1.0419	0.957	0.940
			0.6085	0.875	0.856			
			0.5977	0.942	0.920			
			0.5932	0.960	0.941			
			0.5905	0.968	0.953			

Table 3. *P*−*x*−*y* Data for the R1270 (1) + R1216 (2) System at (313.11, 333.11, and 353.14) K

T = 313.11 K			T = 333.11 K			T = 353.14 K		
P/MPa	x_1	y_1	P/MPa	x_1	y_1	P/MPa	x_1	y_1
1.0994	0	0	1.7882	0	0	2.7782	0	0
1.2254	0.073	0.140	1.9094	0.052	0.086	2.9255	0.049	0.062
1.3273	0.139	0.239	2.0422	0.112	0.170	3.1034	0.111	0.132
1.4314	0.218	0.334	2.1947	0.191	0.266	3.2844	0.183	0.199
1.5250	0.302	0.418	2.3508	0.284	0.362	3.2447	0.168	0.184
1.6271	0.415	0.512	2.5027	0.396	0.464	3.7505	0.986	0.983
1.7123	0.561	0.612	2.6130	0.505	0.552	3.8087	0.960	0.953
1.7493	0.671	0.696	2.6850	0.616	0.640	3.8647	0.930	0.921
1.7597	0.757	0.759	2.7078	0.684	0.696	3.8996	0.910	0.900
1.7579	0.797	0.789	2.7031	0.807	0.797	3.9286	0.890	0.880
1.7488	0.847	0.831	2.6869	0.847	0.832	3.9586	0.868	0.859
1.7308	0.897	0.877	2.6644	0.884	0.868	3.9796	0.848	0.841
1.7208	0.917	0.898	2.6282	0.926	0.910	4.0004	0.826	0.821
1.6982	0.951	0.935	2.5818	0.964	0.953	4.0129	0.811	0.807

Table 4. Model Parameters Regressed for the PR EoS and WS Mixing Rule Incorporating the NRTL Activity Coefficient Model for the R1270 (1) + R1216 (2) System

	T/K					
parameter	263.17	273.16	293.12	313.11	333.11	353.14
τ_{12}/J·mol^{-1}	2142	3231	5109	4088	2177	1949
τ_{21}/J·mol^{-1}	490	881	2069	1342	324	711
k_{ij}	0.1847	0.0410	−0.2038	−0.0565	0.1703	0.1566

Table 5. Mean Relative Deviation (MRD), AAD *U*, and BIAS *U* Obtained in Fitting Experimental VLE Data with PR EoS and WS Mixing Rules Involving the NRTL Model

T/K	BIAS x/%	MRD x/%	BIAS y/%	MRD y/%
263.17	0.47	0.61	−0.41	0.61
273.16	0.54	0.73	−0.65	0.70
293.12	−0.69	0.83	0.26	1.06
313.11	−0.68	0.98	0.26	0.81
333.11	−0.19	0.22	0.00	0.23
353.14	0.10	0.39	0.50	0.80

The average absolute deviation, AAD *U*, and the BIAS *U*, applied on liquid- and vapor-phase mole fractions, are defined by:

$$\text{AAD } U = (100/N)\sum |(U_{\text{cal}} - U_{\text{exp}})/U_{\text{exp}}| \qquad (6)$$

$$\text{BIAS } U = (100/N)\sum ((U_{\text{exp}} - U_{\text{cal}})/U_{\text{exp}}) \qquad (7)$$

where N is the number of data points and $U = x_1$ or y_1.

These indicators, which give information about the agreement between model and experimental results, are presented in Table 5.

It can be seen that the azeotrope disappears for temperatures below the critical temperature of the lightest component. It is particular to the type I systems presenting an azeotrope. For example, the system R32 + propane has the same behavior (Coquelet et al.[10]). Equations 8 and 9 give the evolution of the pressure of the azeotrope with the temperature and the azeotropic composition. Figure 2 shows the logarithm of the azeotropic pressure as a function:

$$\ln(P/\text{MPa}) = -2266.887 \cdot \frac{\text{K}}{T} + 7.8061 \qquad (8)$$

$$(P/\text{MPa}) = 221.066x_{\text{azeo}}^2 - 372.737x_{\text{azeo}} + 157.351 \qquad (9)$$

Conclusions

VLE data are presented at six temperatures for R1216 + R1270. Measurements were undertaken using a “static−analytic” method using the ROLSI samplers. The data are correlated with the PR EoS and the WS mixing rules incorporating the NRTL model. The experimental results are given with the following

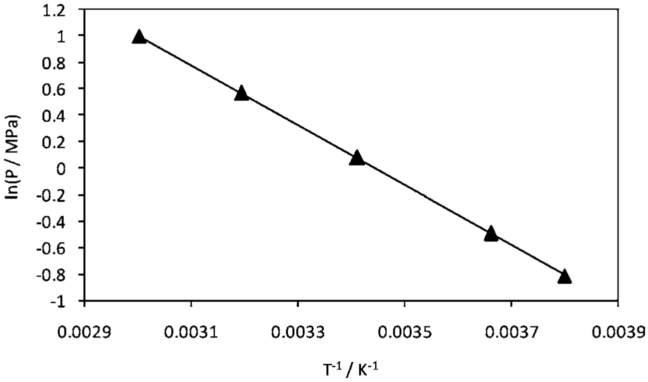

Figure 2. Plot of the logarithm of the azeotropic pressure as a function of $1/T$.

uncertainties: ± 0.02 K, ± 0.0005 MPa, and less than ± 4.0 % for vapor and liquid mole fractions.

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