

# Isothermal VLE Measurements for Difluoromethane + Dimethyl Ether and an Evaluation of Hydrogen Bonding

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Vapor–liquid equilibria (VLE) data for the difluoromethane (R32) + dimethyl ether (RE170) system were measured with the aim of completing our study of hydrogen bonding between hydrofluorocarbons (HFCs) and dimethyl ether. The measurements were taken in an apparatus based on a static analytical method at temperatures ranging between (258.15 and 293.15) K. The R32 + RE170 system shows a slight negative deviation from Raoult's law that is attributed to hydrogen bonding between RE170 and R32. This H bonding was estimated using the homomorphic concept. The physical interaction was represented by the difference between the excess Gibbs energy ( $g^E$ ) of R32 + RE170 and its corresponding homomorphic system, the R32 + propane (R290) system. The VLE data were reduced by means of the Carnahan–Starling–De Santis (CSD) equation of state (EoS) together with the classical mixing rule and then by means of the Redlich–Kwong–Soave (RKS) EoS, with the Huron–Vidal mixing rule, using the NRTL equation for  $g^E$  at infinite pressure. VLE data for the R32 + RE170 system are not reported elsewhere in the literature.

## Introduction

Several vapor–liquid equilibria (VLE) measurements have been performed in our laboratory on RE170 + HFC systems,<sup>1–6</sup> with the aim to provide new information on possible refrigerant mixtures of a new generation and on the intermolecular interactions in blends containing partially fluorinated hydrocarbons, paying special attention to the H bonding. Following these studies, the VLE data for the difluoromethane (R32) + dimethyl ether (RE170) system were measured at temperatures of (258.15, 273.15, and 293.15) K using a static analytical method.<sup>7</sup> In fact, it is also expected that the R32 + RE170 system may form H bonds whose strength can be evaluated by applying the homomorphic concept<sup>8,9</sup> using the experimental VLE data presented here in combination with the homomorphic R32 + propane (R290) system.

The VLE data for the R32 + R290 system at temperatures ranging between 248.13 and 294.91 K have been published by Bobbo et al.<sup>10</sup> The R32 + RE170 system VLE data were regressed by means of the Carnahan–Starling–De Santis (CSD)<sup>11</sup> equation of state (EoS) together with the classical mixing rule and then by means of the Redlich–Kwong–Soave (RKS)<sup>12</sup> EoS, with the Huron–Vidal mixing rule,<sup>13</sup> using the NRTL equation<sup>14</sup> for  $g^E$  at infinite pressure. VLE data for the R32 + RE170 system have not been published in the literature. On the contrary, several VLE data can be found in the literature for the R32 + R290 system.<sup>10,15–20</sup>

## Experimental Section

**Materials.** R32 was supplied by Ausimont with a declared purity of >99.99%; RE170, by Aldrich with a

declared purity of >99%; and R290, by Air Liquide with a declared purity of >99.95%. In all of the reagents, no impurities were detected by gas chromatography using either a flame ionization (FID) or a thermal conductivity (TCD) detector. To facilitate the elimination of the non-condensable gases, each sample underwent several cycles of freezing with liquid nitrogen, evacuation, thawing, and ultrasound.

**Apparatus.** The experimental apparatus has been described in more detail by Bobbo et al.,<sup>7</sup> so here only a brief description is given. Equilibrium is reached in a stainless steel cell of about 50 cm<sup>3</sup> equipped with two glass windows for the visual observation of the mixture and supplied with a magnetic pump to force the vapor through the liquid in order to get to equilibrium more quickly. The composition of the liquid and vapor phases is measured by a gas chromatograph (Hewlett-Packard 6890) connected in line to the equilibrium cell. The FID detector is carefully calibrated by means of gravimetrically prepared mixtures. The uncertainty in the composition measurement is estimated to be within  $\pm 0.003$  in mole fraction for both the liquid and the vapor phases. The temperature measurements are performed by means of a 100- $\Omega$  platinum resistance thermometer connected to a multimeter (Hewlett-Packard 3458) and continuously recorded during the measurements. The temperature stability is of about  $\pm 1$  mK, thanks to a 100-L thermostatic bath controlled by a PID control system. The temperature accuracy is estimated to be  $\pm 0.02$  K. The pressure is measured by means of a Ruska 6000 pressure gauge, with a full scale of 3500 kPa and an accuracy of  $\pm 1$  kPa.

## Results and Discussion

**Experimental Data.** The  $P$ ,  $x$ ,  $y$  equilibrium data for the R32 + RE170 system, measured at temperatures of (258.15, 273.15, and 293.15) K, are presented in Table 1,

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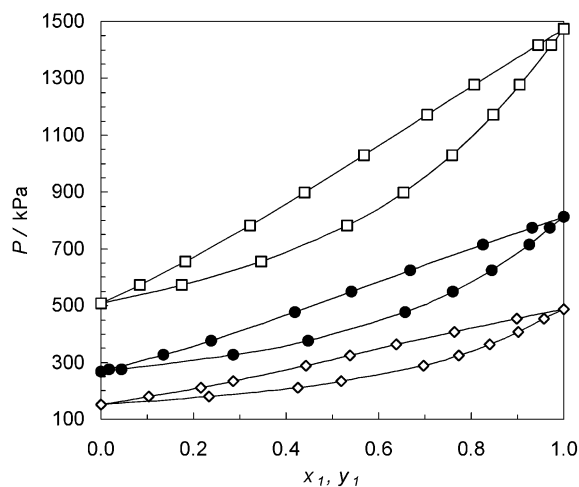
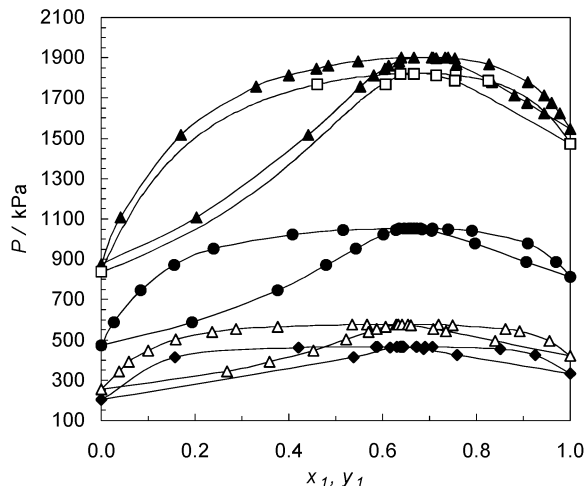
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**Table 1. Experimental Vapor–Liquid Equilibrium Data for the R32 (1) + RE170 (2) System**

$T = 258.15$ K			$T = 273.15$ K			$T = 293.15$ K		
$x_{1,\text{exptl}}$	$y_{1,\text{exptl}}$	$P_{\text{exptl}}/\text{kPa}$	$x_{1,\text{exptl}}$	$y_{1,\text{exptl}}$	$P_{\text{exptl}}/\text{kPa}$	$x_{1,\text{exptl}}$	$y_{1,\text{exptl}}$	$P_{\text{exptl}}/\text{kPa}$
0.0000	0.0000	152.9	0.0000	0.0000	266.8	0.0000	0.0000	509.3
0.1025	0.2330	179.4	0.0181	0.0444	275.0	0.0836	0.1749	573.2
0.2160	0.4247	211.8	0.1356	0.2854	326.8	0.1831	0.3460	654.7
0.2850	0.5198	233.7	0.2378	0.4471	376.2	0.3215	0.5310	782.3
0.4423	0.6965	289.3	0.4195	0.6571	477.2	0.4400	0.6534	898.8
0.5376	0.7727	325.8	0.5405	0.7606	548.9	0.5675	0.7580	1030.4
0.6386	0.8404	362.4	0.6687	0.8451	624.5	0.7048	0.8479	1172.0
0.7639	0.9021	407.7	0.8258	0.9254	713.6	0.8069	0.9046	1277.9
0.8983	0.9578	453.4	0.9313	0.9702	773.3	0.9441	0.9727	1416.3
1.0000	1.0000	488.1	1.0000	1.0000	814.0	1.0000	1.0000	1474.6

**Figure 1.** Vapor–liquid equilibrium for the R32 (1) + RE170 (2) system at  $\diamond$ , 258.15;  $\bullet$ , 273.15; and  $\square$ , 293.15 K.**Figure 2.** Vapor–liquid equilibrium for the R32 (1) + R290 (2) system at  $\blacklozenge$ , 248.13;  $\triangle$ , 254.15;  $\bullet$ , 273.15;  $\square$ , 293.15; and  $\blacktriangle$ , 294.91 K.

whereas the vapor- and liquid-phase saturation boundaries are shown in Figure 1. The system is almost ideal, even if it shows a slight negative deviation from Raoult's law. In Figure 2, the saturation boundaries for the R32 + R290 system are shown. The VLE experimental data for the mixture have been reported elsewhere.<sup>10</sup> There is an evident positive deviation from Raoult's law for the R32 + R290 system, with the presence of an azeotrope at about 0.6 R32 molar fraction.

**Data Reduction.** As a first attempt, the R32 + RE170 system VLE data were correlated by means of the Carnahan–Starling–De Santis (CSD) equation of state (EoS)<sup>11</sup> using the classic mixing rules with only a single interaction

**Table 2. Results of VLE Data Reduction for the R32 + RE170 System by Means of the CSD EoS Together with the Classical Mixing Rule**

$T = 258.15$ K					
$x_{1,\text{exptl}}$	$y_{1,\text{calcd}}$	$P_{\text{calcd}}/\text{kPa}$	$\Delta y$	$\Delta P\%$	$k_{ij}$
0.0000	0.0000	152.6	0.0000	0.19	
0.1025	0.2410	182.0	0.0080	-1.43	
0.2160	0.4368	215.9	0.0121	-1.91	
0.2850	0.5308	237.2	0.0110	-1.49	
0.4423	0.6969	287.9	0.0004	0.49	-0.0146
0.5376	0.7738	320.0	0.0011	1.78	
0.6386	0.8411	355.2	0.0007	2.00	
0.7639	0.9086	400.2	0.0065	1.85	
0.8983	0.9655	449.8	0.0077	0.80	
1.0000	1.0000	487.7	0.0000	0.09	
		bias	0.0059	0.23	
		AAD	0.0059	1.20	
$T = 273.15$ K					
$x_{1,\text{exptl}}$	$y_{1,\text{calcd}}$	$P_{\text{calcd}}/\text{kPa}$	$\Delta y$	$\Delta P\%$	$k_{ij}$
0.0000	0.0000	267.2	0.0000	-0.16	
0.0181	0.0459	275.6	0.0015	-0.23	
0.1356	0.2919	331.5	0.0065	-1.45	
0.2378	0.4521	382.0	0.0050	-1.53	
0.4195	0.6595	476.2	0.0024	0.21	-0.0106
0.5405	0.7612	542.1	0.0006	1.23	
0.6687	0.8472	614.8	0.0021	1.55	
0.8258	0.9301	707.4	0.0047	0.86	
0.9313	0.9748	771.4	0.0046	0.25	
1.0000	1.0000	813.3	0.0000	0.08	
		bias	0.0034	0.08	
		AAD	0.0034	0.76	
$T = 293.15$ K					
$x_{1,\text{exptl}}$	$y_{1,\text{calcd}}$	$P_{\text{calcd}}/\text{kPa}$	$\Delta y$	$\Delta P\%$	$k_{ij}$
0.0000	0.0000	510.7	0.0000	-0.28	
0.0836	0.1801	579.5	0.0052	-1.10	
0.1831	0.3508	664.1	0.0048	-1.43	
0.3215	0.5337	786.5	0.0027	-0.54	
0.4400	0.6555	896.2	0.0021	0.29	-0.0106
0.5675	0.7614	1019.4	0.0034	1.07	
0.7048	0.8538	1158.2	0.0059	1.18	
0.8069	0.9113	1265.4	0.0067	0.98	
0.9441	0.9767	1414.6	0.0040	0.12	
1.0000	1.0000	1476.8	0.0000	-0.15	
		bias	0.0043	0.01	
		AAD	0.0043	0.71	

parameter  $k_{ij}$  and the pure-fluid coefficients taken from ref 21. The results of the data regression with the CSD EoS are shown in Table 2.

Even if the CSD EoS correlates well with the experimental data, with an absolute average deviation of 0.004 in terms of the vapor-phase composition (AAD( $\Delta y$ )) and 0.9% in terms of the saturated pressure (AAD( $\Delta P\%$ )), the deviations show an S-shaped trend.

Then, the RKS EoS<sup>12</sup> combined with the Huron–Vidal<sup>13</sup> mixing rule (HV), where the  $g^E$  at infinite pressure was

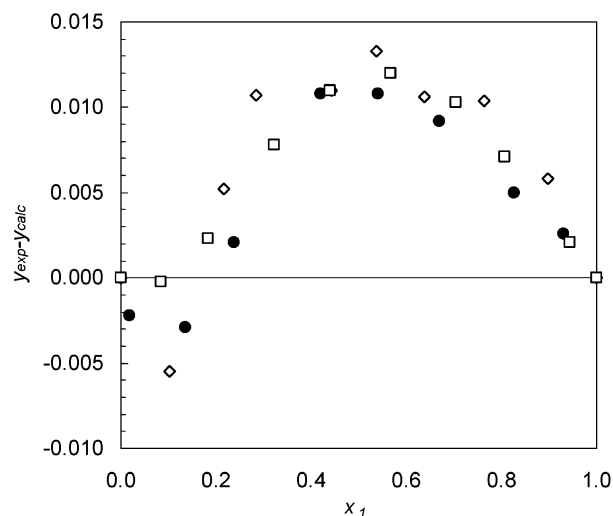
**Table 3.** Results of VLE Data Reduction for the R32 + RE170 System by Means of the RKS–HV–NRTL Model ( $\alpha = 0.3$ )

$T = 258.15 \text{ K}$						
$x_{1,\text{exptl}}$	$y_{1,\text{calcd}}$	$P_{\text{calcd}}/\text{kPa}$	$\Delta y$	$\Delta P\%$	$\Delta g_{12}/\text{J mol}^{-1}$	$\Delta g_{21}/\text{J mol}^{-1}$
0.0000	0.0000	153.7	0.0000	-0.53		
0.1025	0.2275	179.3	-0.0055	0.06		
0.2160	0.4299	212.0	0.0052	-0.09		
0.2850	0.5305	234.0	0.0107	-0.14		
0.4423	0.7075	289.1	0.0110	0.05		
0.5376	0.7860	324.7	0.0133	0.33	-2971.4	4783.7
0.6386	0.8510	362.7	0.0106	-0.09		
0.7639	0.9125	408.4	0.0104	-0.18		
0.8983	0.9636	453.9	0.0058	-0.11		
1.0000	1.0000	487.0	0.0000	0.23		
		bias	0.0077	-0.05		
		AAD	0.0091	0.18		
$T = 273.15 \text{ K}$						
$x_{1,\text{exptl}}$	$y_{1,\text{calcd}}$	$P_{\text{calcd}}/\text{kPa}$	$\Delta y$	$\Delta P\%$	$\Delta g_{12}/\text{J mol}^{-1}$	$\Delta g_{21}/\text{J mol}^{-1}$
0.0000	0.0000	268.6	0.0000	-0.67		
0.0181	0.0422	275.8	-0.0022	-0.30		
0.1356	0.2825	326.8	-0.0029	-0.01		
0.2378	0.4492	376.8	0.0021	-0.15		
0.4195	0.6679	476.5	0.0108	0.15		
0.5405	0.7714	548.0	0.0108	0.17	-2940.8	4574.4
0.6687	0.8543	624.7	0.0092	-0.03		
0.8258	0.9304	715.6	0.0050	-0.28		
0.9313	0.9728	773.9	0.0026	-0.07		
1.0000	1.0000	811.6	0.0000	0.30		
		bias	0.0044	-0.09		
		AAD	0.0057	0.21		
$T = 293.15 \text{ K}$						
$x_{1,\text{exptl}}$	$y_{1,\text{calcd}}$	$P_{\text{calcd}}/\text{kPa}$	$\Delta y$	$\Delta P\%$	$\Delta g_{12}/\text{J mol}^{-1}$	$\Delta g_{21}/\text{J mol}^{-1}$
0.0000	0.0000	510.3	0.0000	-0.20		
0.0836	0.1747	573.3	-0.0002	-0.03		
0.1831	0.3483	655.6	0.0023	-0.13		
0.3215	0.5388	781.6	0.0078	0.09		
0.4400	0.6644	898.4	0.0110	0.05		
0.5675	0.7700	1029.7	0.0120	0.07	-2941.7	4456.9
0.7048	0.8582	1173.1	0.0103	-0.09		
0.8069	0.9117	1278.3	0.0071	-0.03		
0.9441	0.9748	1417.3	0.0021	-0.07		
1.0000	1.0000	1474.3	0.0000	0.02		
		bias	0.0065	-0.03		
		AAD	0.0066	0.08		

represented by the NRTL<sup>14</sup> equation, was applied. In the RKS–HV–NRTL model, only two parameters were regressed, with  $\alpha = 0.3$ . The results of this regression are given in Table 3 and in Figures 3 and 4, where the deviations of the experimental data from the model are shown in terms of the vapor-phase composition and saturated pressure, respectively. The RKS–HV–NRTL model is able to represent the experimental data with  $\text{AAD}(\Delta y) = 0.0071$  and  $\text{AAD}(\Delta P\%) = 0.16\%$ . All of the shown parameters are rounded to the significant digit.

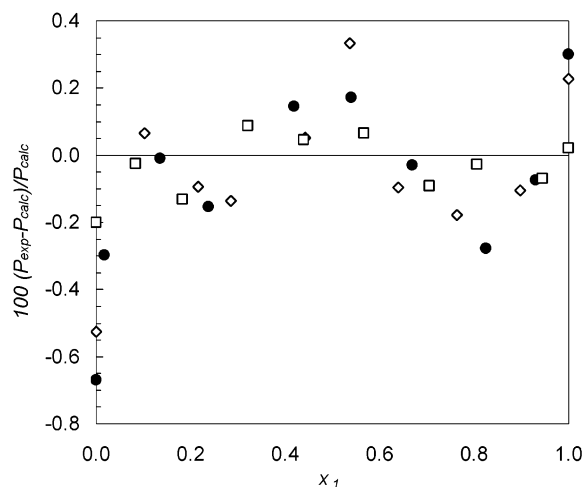
**Comparison with Literature Data.** Other experimental VLE data for the R32 + RE170 system have not been found in the literature by the authors.

On the contrary, several papers were published on the phase equilibria of the R32 + R290<sup>10,15–20</sup> system. Three of them<sup>15–17</sup> have been compared with ours<sup>10</sup> on the basis of the RKS–HV–NRTL model that was used as a reference, taking  $\alpha = 0.3$  a priori. Every set of data measured by different authors was correlated by means of this model, obtaining different set of regressed parameters. In particular, the absolute average deviations (AAD) of the data published by Bobbo et al.<sup>10</sup> from the RKS–HV–NRTL model were about 0.0040 in terms of the vapor-phase composition and 0.2% in terms of the saturated pressure, and they were the lowest among all the other literature data.<sup>15–17</sup>



**Figure 3.** Deviations of the vapor-phase composition for the R32 (1) + RE170 (2) system from the RKS–HV–NRTL model at  $\diamond$ , 258.15;  $\bullet$ , 273.15; and  $\square$ , 293.15 K.

Here, a comparison with data published after Bobbo et al.<sup>10</sup> is performed. Both Coquelet et al.<sup>19</sup> and Kim et al.<sup>20</sup> found good agreement with data from Bobbo et al.<sup>10</sup> on the basis of different models—the RKS–HV–NRTL with the



**Figure 4.** Deviations of the saturated pressure for the R32 (1) + RE170 (2) system from the RKS–HV–NRTL model at  $\diamond$ , 258.15;  $\bullet$ , 273.15; and  $\square$ , 293.15 K.

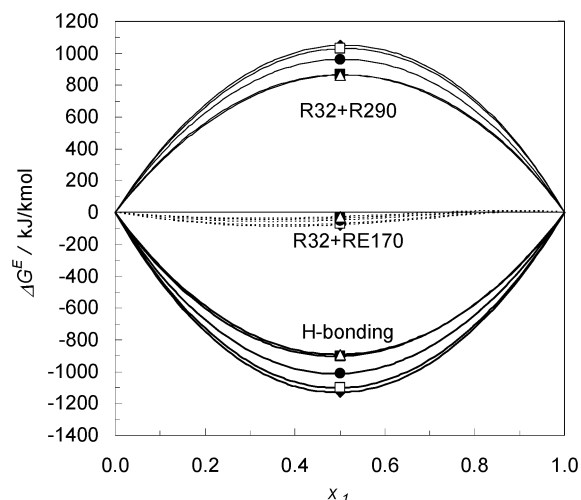
Mathias–Copeman  $\alpha$  function<sup>22</sup> in the RKS EoS for Coquelet et al.<sup>19</sup> and the Peng Robinson (PR)<sup>23</sup> EoS with the classical mixing rule for Kim et al.,<sup>20</sup> respectively. These results are confirmed here on the basis of the RKS–HV–NRTL model. Lee et al.<sup>18</sup> did not consider data from Bobbo et al.<sup>10</sup> for comparison.

The RKS–HV–NRTL model well describes data from Coquelet et al.,<sup>19</sup> with the AAD being within 0.0030 in terms of the vapor-phase composition and 0.3% in terms of the saturated pressure. The deviations in the data from Kim et al.<sup>20</sup> are a little bit higher, with absolute average deviations of 0.0060 in terms of the vapor molar fraction and 0.57 in terms of the saturated pressure percentage deviation, with maximum deviations of 0.02 in terms of the vapor composition and 3% in terms of the saturated pressure. The data from Lee et al.<sup>18</sup> are well represented by the RKS–HV–NRTL model in terms of saturated pressure, with AAD = 0.44%, but show higher deviations in terms of the vapor-phase composition, with AAD = 0.0133.

**Evaluation of H Bonding.** The homomorph concept<sup>8,9</sup> was applied to evaluate the strength of the H bonding between R32 and RE170. On the basis of this method, the  $g^E$  of the R32 + RE170 system is given by the sum of two terms—one given by the H bonding and the other given by a “physical” contribution of the molecular interactions. Considering the molecular interactions in a homomorph system (i.e., R32 + R290), we can calculate this “physical” contribution, assuming it is of the same order as those in R32 + R290. In fact, R290, being nonpolar and having very similar molecular dimensions to RE170, can be considered to be its homomorph. Then, a good approximation of the H-bonding contribution to  $g^E$  for the R32 + R290 system can be calculated as the difference between the  $g^E$  of the R32 + RE170 system and the  $g^E$  of the respective homomorph system R32 + R290, representing only the physical contribution:

$$g_{\text{H bonding}}^E = g_{(\text{R32+RE170})}^E - g_{(\text{R32+R290})}^E \quad (1)$$

Considering the fact that the VLE data for the two systems, R32 + RE170 and R32 + R290, were measured at different temperatures, the excess Gibbs energy for the R32 + RE170 system was calculated at the five experimental temperatures measured for the system with R290 for uniformity. For the isotherms (248.15, 254.15, and



**Figure 5.** Calculated excess Gibbs energy for the two homomorph R32 (1) + R290 (2) and R32 (1) + RE170 (2) systems at  $\diamond$ , 248.13;  $\square$ , 254.15;  $\bullet$ , 273.15;  $\triangle$ , 293.15; and  $\blacksquare$ , 294.91 K.  $g^E$  of the R32 + R290 system (—) and of the R32 + RE170 system (···) calculated with the RKS–HV–NRTL EoS and H bonding evaluated as the difference between the  $g^E$  values of the two homomorph systems (–).

294.15 K), the needed values of the parameters for the R32 + RE170 system were obtained by linear interpolation. The  $g^E$  was estimated by means of the regressed RKS–HV–NRTL model by the equation

$$g^E = RT(\ln \phi - \sum x_i \ln \phi_i) \quad (2)$$

where  $\phi$  and  $\phi_i$  are the fugacity coefficients of mixtures and pure components, respectively, at the same temperature,  $T$ , and pressure,  $P$ , and  $R$  is the gas constant. At temperatures different from the experimental condition, the RKS–HV–NRTL parameters were estimated by considering their dependence on temperature. Figure 5 shows the results of this calculation.

The results of this study confirm that R32 has active proton donors that are able to form H bonds with proper proton acceptors. The physical contribution to the intermolecular interaction for the R32 + RE170 system seems to be very important, being opposite in sign to the H-bonding contribution.

## Conclusions

VLE data for the R32 + RE170 system were measured at 258.15, 273.15, and 293.15 K. This system shows almost ideal behavior, with a small deviation from Raoult’s law. The experimental  $T$ ,  $P$ ,  $x$ ,  $y$  VLE data are well represented by both the CSD EoS with the classical mixing rule and the RKS–HV–NRTL model, even if better results are achieved by the latter. This model is used to estimate the excess Gibbs energy and to study the molecular interaction between the two molecules. For this purpose, the homomorph concept is used, evaluating the physical contribution from the  $g^E$  of the homomorph R32 + R290 system. The results confirm the formation of hydrogen bonds between R32 and RE170. A comparison with the last available literature data for the R32 + R290 system was performed on the basis of the RKS–HV–NRTL model. Good agreement with the published data was found.

## List of Symbols

$k_{ij}$  = interaction parameter in the CSD EoS  
 $P$  = pressure (kPa)

$R$  = ideal gas constant  
 $T$  = temperature (K)  
 $x$  = liquid mole fraction  
 $y$  = vapor mole fractions  
 $\Delta g_{12}$ ,  $\Delta g_{21}$  = NRTL equation parameters  
 $\alpha$  = NRTL equation parameter  
 Subscripts  
 1 = low-boiling mixture component  
 exptl = experimental property  
 calccd = calculated property  
 $i, j$  = one mixture component  
 Superscript  
 E = excess property

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