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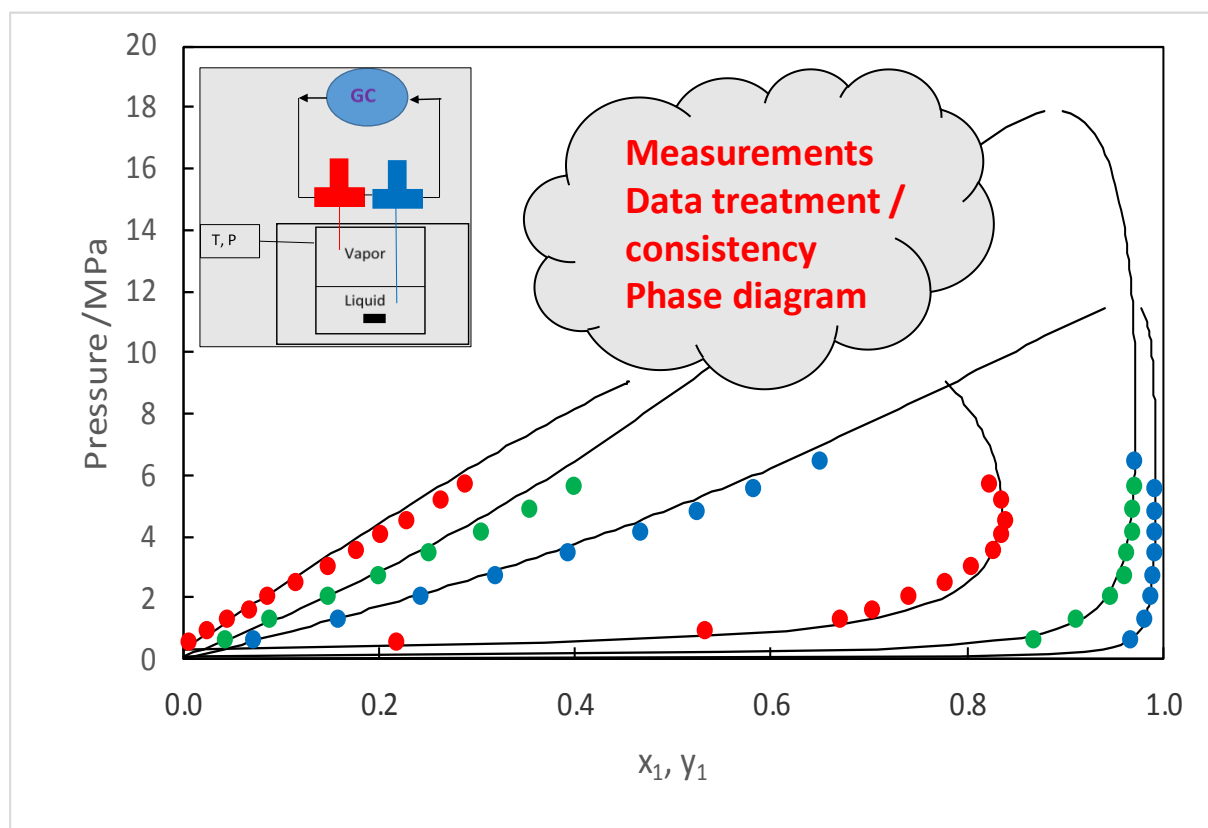
Vapor liquid equilibrium data for the hydrogen chloride – Chlorobenzene binary system at 353.16, 403.16 and 453.25 K

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Short communication

TOC GRAPHI



Abstract

The study presents p - T - x - y phase equilibria measurements of one solvent, chlorobenzene and one solute, hydrogen chloride. The technique of the equipment used is based on a “static-analytic” method **that takes advantages of two capillary samplers linked to a gas chromatograph**. Measurements were done at three temperatures (353.16, 403.16 and 453.25 K) and pressures from 0.6 up to 6.5 MPa. The experimental data measured were successfully correlated using the Peng Robinson Equation of state.

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1. Introduction

Isocyanates are important intermediates for polymer production like polyurethane. In effect, this polymer is obtained by reaction of addition between a polyol and one diisocyanates¹. Isocyanates are produced by chemical reaction between one amine with phosgene. This reaction is realized in the presence of one solvent, for example chlorobenzene. The products of the chemical reaction are isocyanate and hydrogen chloride. The process require the thermal separation of hydrogen chloride, phosgene and the solvent². The design of the distillation columns requires knowledge on vapour liquid equilibria (VLE) of hydrogen chloride + chlorobenzene binary system and a good knowledge of its phase diagram. In chemical engineering, an accurate knowledge of phase diagrams is strongly required for the design and process simulation of separation units like distillation and extraction³ column. Thermodynamic models (like equations of state and activity coefficient models) that generally contain several empirical parameters are implemented in process simulation software. In the common engineering practice, the values of the thermodynamic model binary interaction parameters are obtained after adjustment on different sets of experimental data such as vapor–liquid or liquid–liquid equilibria (VLE, LLE, etc.), of the system of interest. Measurements of accurate experimental data require efficient experimental setup and adequate experimental procedure.

A summary of the data founded in the literature for the hydrogen chloride (1) – Chlorobenzene (2) system is presented in Table 1. As can be seen, the data found in the open literature correspond to the liquid molar fraction of hydrogen chloride in the conditions of HCl dilution, i.e. for compositions low in HCl ($x_{\text{HCl}} < 8\%$ mole fraction). It is obvious that from these data (low equilibrium pressure and low liquid composition), it will be difficult to determine the totality of the phase diagram and to adjust the parameters of a thermodynamic model in order to predict the totality of the phase diagram. In 2011, Huang et al.⁹ have used molecular simulation to generate three isotherms at 283.15, 393.15 and 423.15 K. In this paper, new set experimental data of the Hydrogen chloride + Chlorobenzene binary system are presented at 353.16, 403.16 and 453.25 K.

[Table 1]

Table 1: Literature VLE data of Hydrogen chloride (1) – Monochlorobenzene (2) system.

References	Number of data points	Temperature range/K	Pressure range/bar	Liquid molar fraction /x ₁	Vapour molar fraction /y ₁
O'Brien et al. ⁴	6	298.15	0.0401-0.453	0.000911-0.01147	--
O'Brien et al. ⁵	11	303.15 – 313.15	0.03-0.34	0.0058-0.0726	--
Gerrard et al. ⁶	6	273.15-315.15	1	0.0185-0.0561	--
Ahmed et al. ⁷	2	293.15-298.15	1	0.0250-0.0314	--
Zetkin et al. ⁸	6	283.15-333.15	1.01	0.0148-0.0407	--

2. Experimental

2.1. Materials

The sources and the qualities of the used chemicals, as certified by the manufacturers, are presented in Table 2. Apart from a careful degassing of Chlorobenzene, no further purification or pre-treatment were performed.

[Table 2]

Table 2: Chemical sample table.

Chemical name	CAS number	Source	Initial purity (vol %)	Purification method	Final purity	Analysis method
Chlorobenzene	108-90-7	Acros	≥99.99	None	--	GC
Hydrogen chloride	7647-1-0	Alpha gaz	99.8	None	--	GC

GC: Gas Chromatograph

2.2. Apparatus and Experimental Procedure

The equipment (Figure 1) used was previously described by Coquelet et al.¹⁰⁻¹³. Briefly, the equilibrium cell (volume 30 cm³) is immersed in a thermo-regulated liquid bath (LAUDA RE 212). Two (Pt-100) platinum probes are used to measure the equilibrium temperature. They are calibrated by comparison with a 25 Ω reference platinum probe (Tinsley, France, with an uncertainty $u(T)=0.006K$). The accuracy in the temperature measurements is estimated as ± 0.02 K. Pressure is measured by one pressure transducer DRUCK PTX 611 (0 - 6 MPa) thermostated at 333.15 K by means of a PID regulator (FUJI, model PXE-4). The pressure transducer is calibrated using a dead weight balance (Desgranges & Huot model 5202SCP) in the pressure range (0.1- 5.8 MPa) and the accuracy is estimated to be ± 0.5 kPa.

A data acquisition unit (Agilent 34972A) is used to collect both temperature and pressure signals. At equilibrium condition, two capillary samplers ROLSI^{®14} are used to sample small amount of vapour and liquid phases (few μg). The capillary samplers are connected to a Gas Chromatograph (Varian (model CP 3800)) by a heated transfer line. Samples were analyzed by a thermal conductivity detector (TCD). WINILAB III software (Perichrom, France) is used for peak integration and their analysis.

The calibration of the GC detector is made by introducing known pure component volumes with appropriate syringes (500 μL for Hydrogen chloride and 5 μL for chlorobenzene). The resulting relative accuracies concerning the mole numbers are 5% for Hydrogen chloride and 1% for chlorobenzene, and the maximum standard uncertainty on liquid mole fractions was estimated about 0.013. The packed column (from Restek France) used in the gas chromatograph ($T_{oven}= 220^{\circ}C$ and Helium carrier gas flow: 25 ml.min⁻¹) is a 5% Krytox on Carbolack B (60/80 mesh, 1.5 m X 1/8" Silcosteel) column

The expression (Eq. 1) for the calculation of the uncertainty of mixture composition of component i is

$$u_{cal}(x_i) = \sqrt{\sum_j^{n_{comp}} \left(\frac{\partial x_i}{\partial n_j} \right)^2 u^2(n_j)} \quad (1)$$

Consequently, for a binary system, one can calculate uncertainty on mole fraction x_1 by Eq.

$$(2) \cdot u_{cal}(x_1) = x_1(1-x_1) \sqrt{\left(\frac{u(n_1)}{n_1}\right)^2 + \left(\frac{u(n_2)}{n_2}\right)^2}$$

(2)

The combined standard temperature uncertainty, $u(T)$ would be:

$$u(x_i) = \pm \sqrt{u_{calib}(x_i)^2 + u_{rep}(x_i)^2}$$

(3)

With u_{calib} uncertainty due to TCD calibration and u_{rep} uncertainty due to the repeatability of the measurement.

[Figure 1]

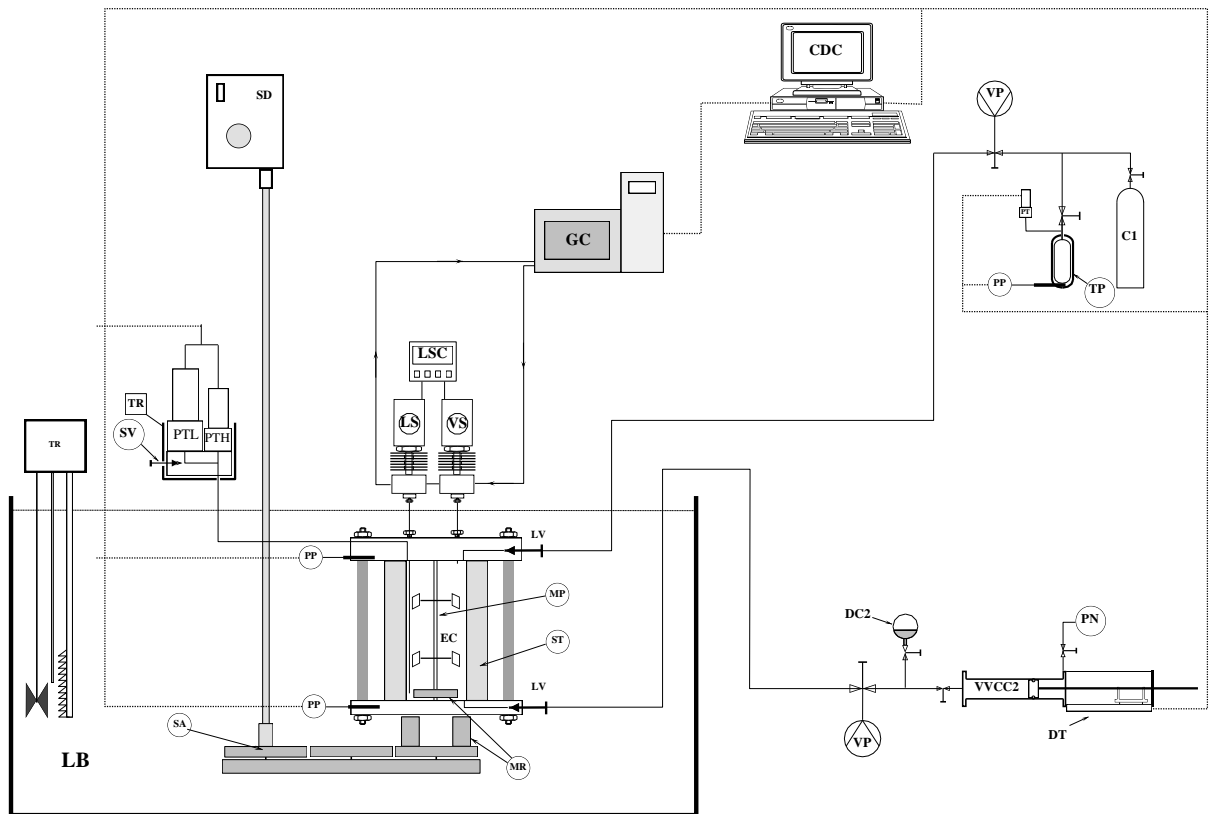


Figure 1: Experimental setup « analytic-static » with two online capillary samplers ROLSI®

C1: Gaz cylinder for component 1; CDC: Central Desktop Computer; DC2: Degassed Component 2; DT: Displacement Transducer; EC: Equilibrium Cell; GC: Gas Chromatograph; LB: Liquid Bath; LS: Liquid Sampler; LSC: Local Sample Controller; LV: Loading Valve; MR: Magnetic Rod; MP: Multiple Phase Agitator; PN: Pressurized Nitrogen; PP: Platinum Probe; PT: Pressure Transducer (L: Low pressure; H: High pressure); SA:

Stirring Assembly; SD: Stirring Device; ST/ Sapphire Tube; SV: Separation Valve; TP: Thermal Press; TR: Thermal Regulator; VP: Vacuum Pump; VS: Vapor Sampler; VVC2: Variable Volume Cell for Component 2.

3. Correlation

The critical temperatures (T_c) and pressures (P_c) and acentric factors (ω) for pure Hydrogen chloride and chlorobenzene which are collected from Simulis thermodynamic software (from Prosim, Toulouse, France) are provided in Table 3.

[Table 3]

Table 3. Thermal properties for Hydrogen chloride and chlorobenzene pure component (Source Simulis thermodynamic software)

Component	T_c /K	P_c /MPa	Acentric factor ω
Hydrogen chloride	324.65	8.310	0.131544
chlorobenzene	632.35	4.519	0.249857

Simulis thermodynamic software is used to correlate the experimental VLE data of (HCl + chlorobenzene) system. The Peng-Robinson EoS¹⁵ (Eq. 3), combined with the Wong Sandler mixing rules¹⁶ (Eqs. 4 to 6) involving the NRTL activity coefficient model¹⁷ (Eq. 7) with non-randomness parameter value equal to 0.3, is considered for the data treatment.

$$\left(P + \frac{a(T)}{(v^2 + 2bv - b^2)} \right) (v - b) = RT \quad (3)$$

$$\text{With } a = \Omega_a \frac{R^2 T_c^2}{P_c}, \quad b = \Omega_b \frac{RT_c}{P_c}, \quad \Omega_a = 0.457240, \quad \Omega_b = 0.07780$$

$$\text{And } a(T) = a_c \alpha(T), \quad \alpha(T) = \left[1 + m(1 - T_R^{1/2}) \right]^2 \quad \text{with } m = 0.374640 + 1.542260\omega - 0.26992\omega^2.$$

$$b = \frac{\sum_i \sum_j x_i x_j \left(b - \frac{a}{RT}\right)_{ij}}{1 - \left(\frac{\sum_i x_i \frac{a_i}{b_i}}{RT} + \frac{g^E(T, P = \infty, x_i)}{CRT}\right)} \quad (4)$$

$$b - \frac{a}{RT} = \sum_i \sum_j x_i x_j \left(b - \frac{a}{RT}\right)_{ij} \quad (5)$$

$$\left(b - \frac{a}{RT}\right)_{ij} = \frac{1}{2} \left[\left(b - \frac{a}{RT}\right)_i + \left(b - \frac{a}{RT}\right)_j \right] (1 - k_{ij}) \quad (6)$$

k_{ij} is a binary interaction parameter and $C = \ln(1/2)$.

$$\frac{g^E(T, P, x_1)}{RT} = \sum_i x_i \sum_j \frac{x_j \exp(-\alpha_{ji} \tau_{ji})}{\sum_k x_k \exp(-\alpha_{ki} \tau_{ki})} \tau_{ji} \quad (7)$$

With τ_{ij} the binary interaction parameters. The value of α_{ij} is equal to 0.3.

A bubble pressure objective function is selected to adjust the binary interaction parameters (Eq. 8).

$$F = \frac{100}{N} \left(\sum (p^{exp} - p^{cal})^2 + \sum (y_2^{exp} - y_2^{cal})^2 \right) \quad (8)$$

where N is the number of experimental data points and p_{exp} and p_{cal} are the experimental and calculated bubble pressure and y_2^{exp} and y_2^{cal} are the experimental and calculated chlorobenzene.

4. Results and discussion

The results (experimental and calculated data) are presented in Table 4 (the liquid or vapor composition value corresponds to the average of the composition of the n_x or n_y samples) and plotted on figure 2. In Table 5 are presented the values of the parameters adjusted using our experimental data. The performance of the model used to correlate the experimental data was assessed by means of the following relative deviations, BIAS U and AAD U which are expressed as:

$$AAD U = \frac{1}{N} \sum_{i=1}^N |U_{i,exp} - U_{i,cal}| \quad (9)$$

$$BIAS U = \frac{1}{N} \sum_{i=1}^N (U_{i,exp} - U_{i,cal}) \quad (10)$$

Where U is the pressure (p) or the vapor composition (y_1), N is the number of experimental measurements. Results are presented in Table 5. As we can see, the data are quite well represented by the model. Moreover, we can notice some more important deviations concerning the vapour phase. This is probably due to the difficulties encountered during the step of TCD calibration for HCl and also due to the fact this system is strongly asymmetric (vapor phase very rich in HCl at low temperature). Finally, we can also observe that the region close to the expected mixture critical point is not very predicted by our model. Figure 3 presents the evolution of relative volatility. Figures 4 and 5 present the comparison between the experimental and calculated partition coefficient of HCl and Monochlorobenzene respectively. According to the Figures 3 to 5 we can observed that the prediction obtained using our model reproduce correctly the experimental tendencies for each temperature.

The level of pressure (lower than 1 bar) and the range of studied compositions of literature data presented in Table 1 are not identical to ours. Consequently, it is not possible to use the literature data with our model. In addition, the comparison with molecular simulation data is not easy due to the lack of pseudo-experimental data particularly close to the mixture critical point. However, in order to compare our works with molecular simulation predictions, we have decided to consider a simple model with only one single binary interaction parameter: the Peng Robinson EoS with the classical mixing rule. We have to take into account that this model is not well adapted for the description of VLE close to the mixture critical point (this is why we have used the Wong Sandler Mixing rule for the data treatment of our data). Table 6 presents the obtained results that confirm the weakness of this model. Figure 6 presents the variation of the BIP with the temperature and Figure 7 compares the predicted partition compositions between the molecular simulation data (Huang et al.⁹) and this work. We can observe a quite good agreement between our new data and molecular simulation data. We have also plotted on Figure 3 the relative volatility calculated using molecular simulation data for two temperatures. We can also observed that there is a good agreement between experimental and molecular simulation works.

[Figure 2]

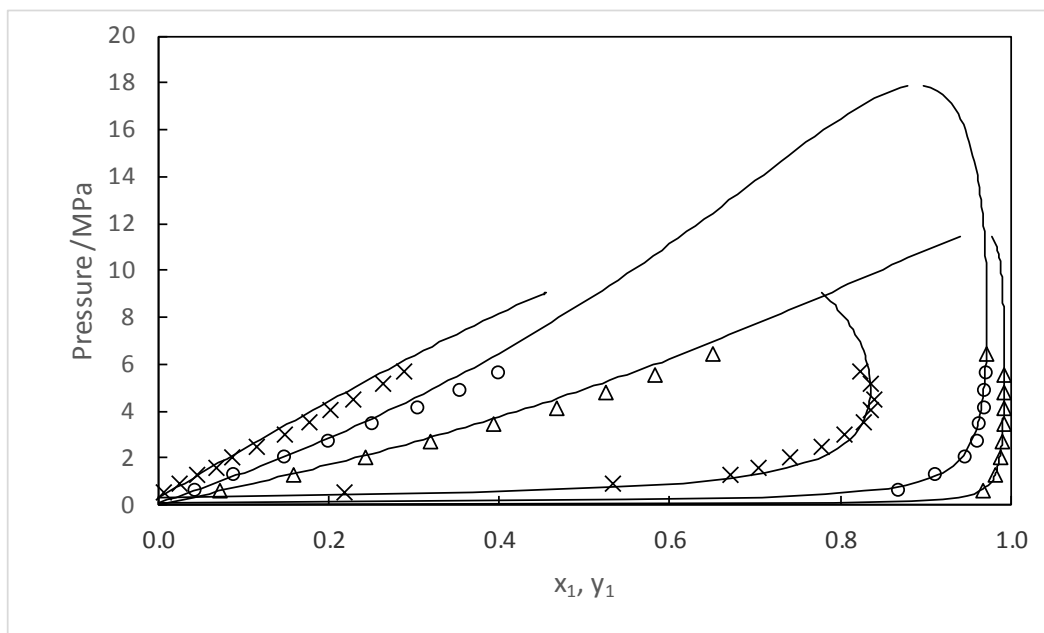


Figure 2: Vapor – Liquid equilibrium isotherms for Hydrogen Chloride (1) + chlorobenzene (2) binary system: (Δ): 353.16 K, (\circ), 403.16 K; (\times): 453.25 K solid lines, calculated results using PR EoS model with Wong Sandler mixing rules involving NRTL activity coefficient model.

[Table 4]

Table 4: Vapor liquid equilibrium of Hydrogen chloride (1) + Chlorobenzene (2) binary system at 353.16, 403.16 and 453.25 K. $u(x_i)$ and $u(y_i)$ are standard uncertainties. Expanded uncertainties ($k=2$): $U(T) = 0.02$ K, $U(p) = 0.5$ kPa

T/K= 353.16										
<i>Experimental data</i>						<i>Calculated data</i>			<i>Deviation</i>	
<i>P / MPa</i>	<i>x₁</i>	<i>n_x</i>	<i>u(x₁)</i>	<i>y₁</i>	<i>n_y</i>	<i>u(y₁)</i>	<i>P / MPa</i>	<i>y₁</i>	$\Delta P/MPa$	Δy_1
0.6316	0.0724	6	0.0034	0.968	5	0.002	0.5992	0.9642	0.0323	-0.0038
1.3128	0.159	7	0.007	0.9820	5	0.0010	1.3427	0.9825	-0.0299	0.0005
2.0137	0.242	6	0.010	0.9877	5	0.0009	2.1121	0.9878	-0.0984	0.0001
2.7190	0.318	6	0.012	0.9905	5	0.0006	2.8708	0.9901	-0.1518	-0.0004
3.4233	0.394	6	0.012	0.9915	6	0.0006	3.6866	0.9914	-0.2634	-0.0001
4.1438	0.467	6	0.013	0.9928	5	0.0005	4.5297	0.9921	-0.3860	-0.0007
4.8219	0.524	6	0.013	0.9929	5	0.0005	5.2323	0.9924	-0.4104	-0.0005
5.5493	0.583	7	0.014	0.9926	5	0.0005	6.0034	0.9925	-0.4541	-0.0001
6.4673	0.651	5	0.013	0.972	5	0.003	6.9506	0.9924	-0.4833	0.0204
T/K= 403.16										
0.6042	0.0429	7	0.0021	0.869	6	0.007	0.6299	0.8371	-0.0257	-0.0319
1.2872	0.0892	7	0.0042	0.913	6	0.006	1.2413	0.9126	0.0458	-0.0004
1.9963	0.1472	6	0.0064	0.9461	7	0.0026	2.0626	0.9433	-0.0664	-0.0028
2.7234	0.200	2	0.008	0.961	6	0.002	2.8672	0.9560	-0.1439	-0.0048
3.4263	0.250	6	0.010	0.964	6	0.002	3.6824	0.9629	-0.2561	-0.0011
4.1571	0.304	6	0.011	0.971	5	0.002	4.6249	0.9675	-0.4679	-0.0032
4.9002	0.354	5	0.014	0.970	4	0.002	5.5587	0.9701	-0.6585	0.0001
5.6132	0.3990	5	0.0124	0.972	6	0.002	6.4522	0.9716	-0.8390	-0.0004
T/K= 453.25										
0.5093	0.0055	4	0.0005	0.218	7	0.011	0.4327	0.2472	0.0766	0.0292
0.8955	0.0251	4	0.0013	0.534	5	0.014	0.8417	0.5784	0.0538	0.0444
1.2673	0.0457	8	0.0023	0.671	6	0.012	1.2705	0.6948	-0.0032	0.0238
1.6077	0.067	9	0.003	0.704	7	0.011	1.7147	0.7524	-0.1070	0.0484
1.9970	0.0869	4	0.0041	0.742	6	0.013	2.1243	0.7829	-0.1273	0.0409
2.4978	0.115	6	0.006	0.779	7	0.012	2.7028	0.8083	-0.2050	0.0293
3.0209	0.147	8	0.006	0.804	5	0.011	3.3567	0.8240	-0.3359	0.0200
3.5248	0.176	7	0.0075	0.828	8	0.009	3.9439	0.8315	-0.4191	0.0035
4.0316	0.202	7	0.0083	0.835	5	0.008	4.4652	0.8347	-0.4336	-0.0003
4.5301	0.2283	7	0.0090	0.840	6	0.007	4.9866	0.8355	-0.4565	-0.0045
5.1581	0.2624	7	0.0099	0.836	7	0.007	5.6523	0.8338	-0.4942	-0.0022
5.6877	0.2883	6	0.0105	0.823	6	0.008	6.1488	0.8306	-0.4612	0.0076

n_x : number of liquid samples, n_y : number of vapor samples

[Table 5]

Table 5: Values of NRTL and Wong Sandler mixing rules binary interaction parameter, BIAS, and AAD of pressure and vapor compositions for the three isotherms.

T/K	τ_{12}	τ_{21}	k_{12}	Bias p/%	Bias y/%	AAD p/%	AAD y/%
353.16	-0.014	68.2	0.4786	-5.4	4.5	6.6	12
403.16	-0.041	125.9	0.5294	-7.1	-7.1	7.9	7.3
453.25	1.502	689.7	0.0465	-5.2	6.5	8.7	7.2

[Table 6]

Table 6: Values of classical mixing rule binary interaction parameter. BIAS and AAD of pressure and vapor compositions for the three isotherms.

Source	T/K	k_{12}	Bias p/%	Bias y/%	AAD p/%	AAD y/%
Huang et al. ⁹	283.15	0.0078	1.7	-0.1	3.6	0.1
	393.15	0.0009	5.4	1.1	5.4	1.1
	423.15	-0.0102	8.8	1.8	8.8	1.8
This work	353.16	-0.0113	-3.1	-0.1	4.2	0.3
	403.16	-0.0101	-5.9	0.8	6.2	0.8
	453.25	-0.0290	7.1	-5.2	7.2	5.7

[Figure 3]

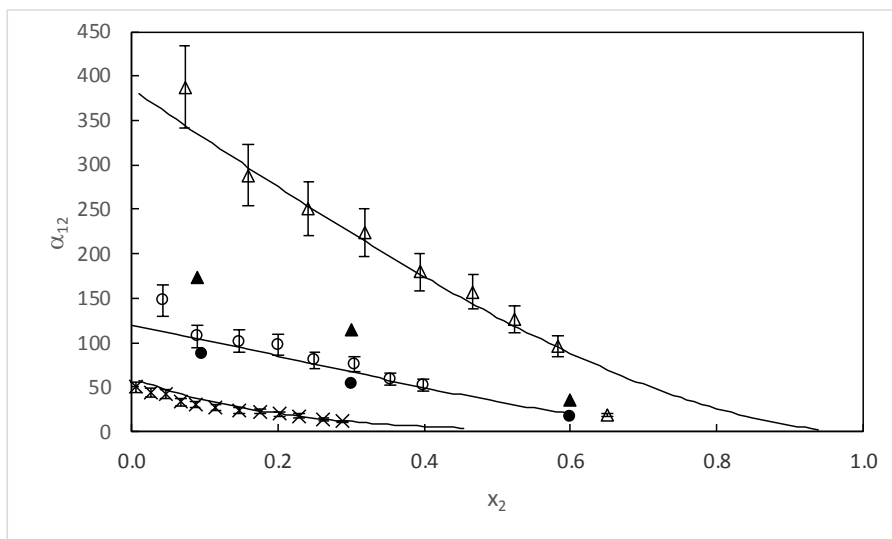


Figure 3: Variation of the relative volatility of Hydrogen Chloride (1) + Chlorobenzene (2) binary system as a function of chlorobenzene composition: (Δ): 353.16 K, (\circ), 403.16 K; (\times): 453.25 K solid lines, calculated results using PR EoS model, Molecular simulation prediction (Huang et al.⁹) \blacktriangle : 393.15 K, \bullet : 423.15 K.

[Figure 4]

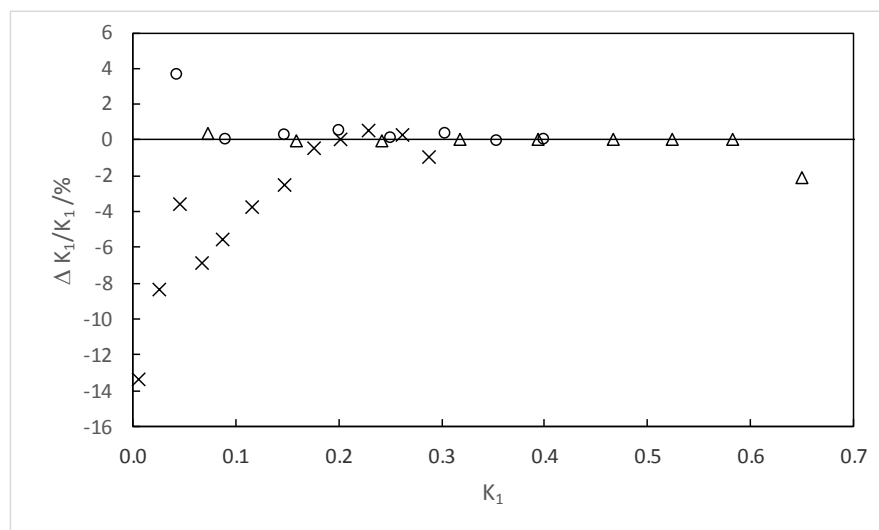


Figure 4: Percentage errors of model K-values of HCl (1). (Δ): 353.16 K, (\circ), 403.16 K; (\times): 453.25 K

[Figure 5]

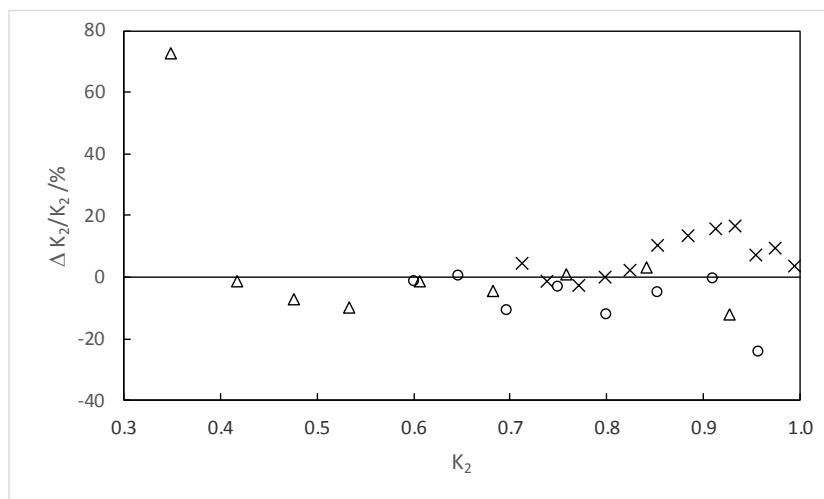


Figure 5: Percentage errors of model K-values of Chlorobenzene (2). (Δ): 353.16 K, (\circ), 403.16 K; (\times): 453.25 K

[Figure 6]

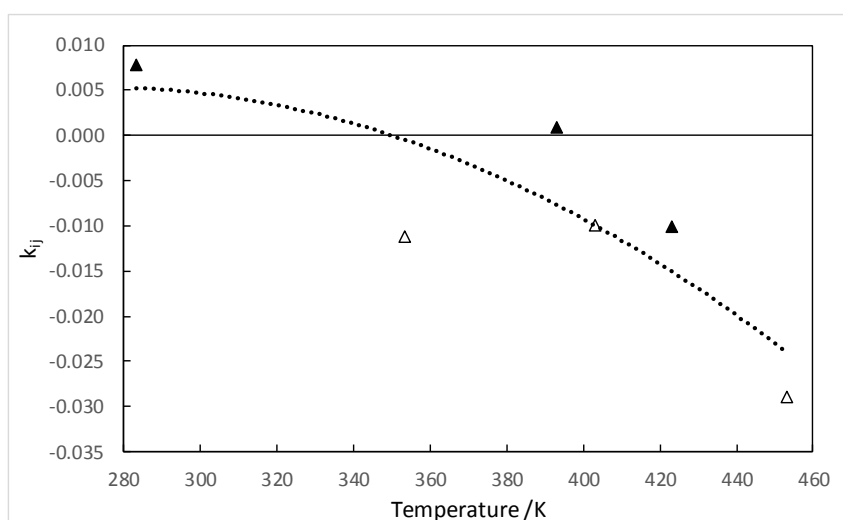


Figure 6: Variation of the Peng-Robinson classical mixing rule binary interaction parameters with the temperature. (\blacktriangle): Huang et al.⁹, (Δ): this work. Dotted line: second order polynomial curve.

[Figure 7]

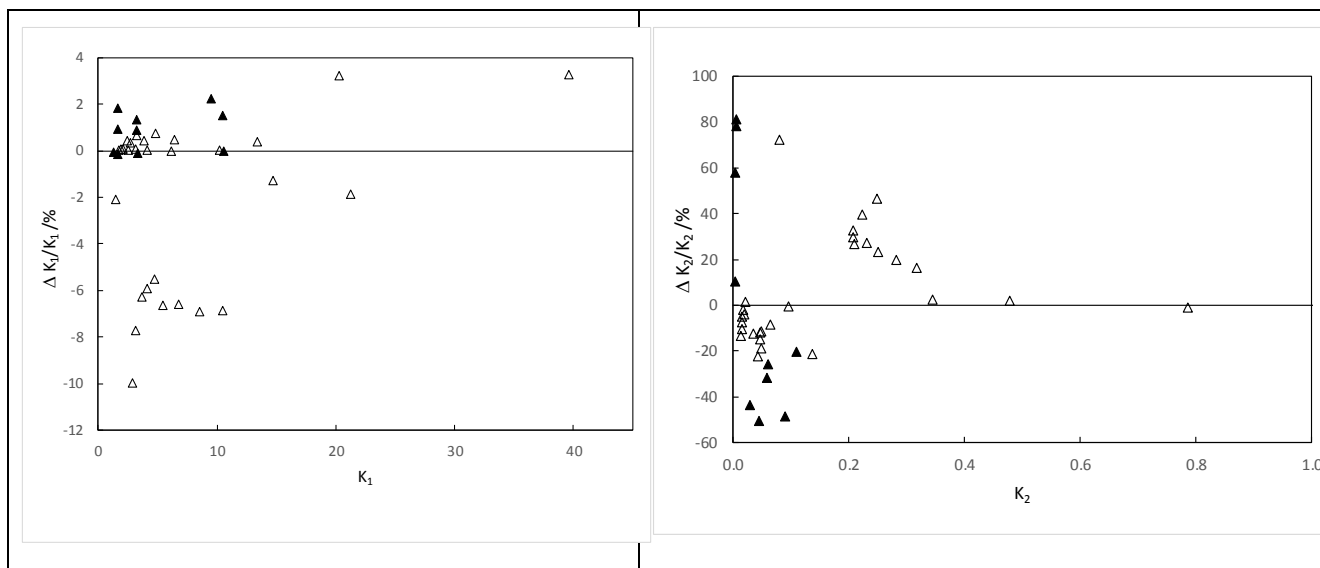


Figure 7: Percentage errors of model K-values of HCl (1) and Chlorobenzene (2). (▲): Huang et al.⁹, (Δ): this work.

5. Conclusions

New vapor liquid equilibrium data of the Hydrogen Chloride (1) + Chlorobenzene binary system were measured using static - analytic apparatus developed in the CTP laboratory. New data measured were correlated using Peng Robinson Equation of state involving Wong Sandler mixing rules and NRTL activity coefficient model. The new data complete the literature data set and show new data for mixture rich in Hydrogen Chloride and at high pressure and high temperature.

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