



# Investigation of Thermodynamic Consistency Test of Carbon Dioxide (CO<sub>2</sub>) in Room-Temperature Ionic liquids using Generic van der Waals Equation of State

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## Abstract

Thermodynamic consistency test of isothermal vapor-liquid equilibrium (VLE) data of various binary systems containing Carbon dioxide (CO<sub>2</sub>)/Room temperature ionic liquids (RTILs) have been investigated in wide ranges of pressures in each isotherm precisely. In this paper Generic van der Waals (GvdW) equation of state (EoS) coupled with modified van der Waals Berthelot mixing rule has successfully been applied for correlating P-T-x binary data. The optimum parameters were obtained by minimizing the average relative deviation between modeled and experimental data based on the bubble pressure algorithm. Modeling is highly shown satisfactory in all cases which means that deviations in correlated data are low subsequently can prove that the flexibility and capability of the proposed model for thermodynamic consistency. Results of the consistency test represented ten isothermal experimental data set to be thermodynamically consistent, fourteen were declared to be not fully consistent and just four isothermal experimental data sets were represented to be thermodynamically inconsistent.

## Keywords:

Carbon Dioxide,  
Equation Of State,  
Generic Van Der Waals,  
Room Temperature Ionic  
Liquids,  
Thermodynamic Consistency  
Test

## Introduction

Ionic liquids or liquid electrolytes which known as green solvents are a new type of solvents with exclusive properties such as insignificant vapor pressure, low viscosity and high thermal stability which has drawn the attention of scientists, thermodynamic researchers and industries [1].

Carbon dioxide which is recognized as a greenhouse gas has adversely affected the atmosphere. For instance, it has contributed to ozone layer depletion and global warming. In order to eliminate carbon dioxide from flue gases, ionic liquids can be a solvent which is able to absorb carbon dioxide with no supplementary processes [2]. The necessity of grabbing carbon dioxide by ionic liquids has generated many investigations on the solubility of CO<sub>2</sub> in ionic liquids [3-5].

In order to represent appropriate thermodynamic models, the accuracy of a set of vapor-liquid equilibrium (VLE) experimental data is a prerequisite. The thermodynamic consistency test is an approach to examine the dependability of a set of experimental data. The most trustable thermodynamic equation that must be satisfied for the consistency test is the Gibbs-Duhem equation. The thermodynamic consistency test declares that if the Gibbs-Duhem equation is not

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obeyed then the *VLE* data are inconsistent which is considered to be incorrect while, If Gibbs-Duhem equation is conformed then the *VLE* data is thermodynamically consistent but not authentic necessarily.

In order to investigate thermodynamic consistency, there are diverse methods based on the mathematical rearrangement of the Gibbs-Duhem equation such as slope test, differential test and integral test as well as tangent–incept test [6].

Valderrama and Robles [7] studied thermodynamic consistency test for high-pressure binary systems which include gas/solid mixtures and developed the method for ternary systems including two solid solutes and a compressed gas. One of the high-pressure mixtures consists of CO<sub>2</sub> and 2,3 dimethylnaphthalene and 2,6 dimethylnaphthalene as solutes. In addition, the other high-pressure mixture encompassing CO<sub>2</sub> as solvent and capsaicin and β-carotene as solutes.

Trejos et al. [8] have modeled polar and non-polar asymmetry mixtures based on the phi-phi approach with applying the Peng-Robinson (PR) equation of state along with Wong-Sandler (WS) mixing rule along with thermodynamic consistency test. Faúndez et al. have also applied thermodynamic consistency test of 25 binary systems consist of H<sub>2</sub>O with congener mixtures like acetic acid, acetaldehyde, ethyl acetate, furfural, methanol, 1-propanol, methyl acetate and 2-butanol with modified version of Peng-Robinson equation of state by Kwak and Mansoori and fundamental Gibbs-Duhem equation for the purpose of testing thermodynamic consistency [9,10]. In another research done by Faúndez et al. [11], the thermodynamic consistency test of experimental solubility of NH<sub>3</sub> (ammonia) in different ionic liquids using Peng-Robinson Kwak and Mansoori equation of state and van der Waals mixing rule have been investigated. They have modeled 47 isothermal *P*-*x* experimental data, given from literature, then they have studied the thermodynamic consistency test and reported the result of the consistency test clearly. Eslamimanesh et al. [12] have applied Peng-Robinson and Soave-Redlich-Kwong equations of state associated to van der Waals type one (vdW1), van der Waals type two (vdW2) and Wong-Sandler (WS) mixing rules for modeling the solubility of supercritical CO<sub>2</sub> in ionic liquids to study the thermodynamic consistency test. They found Peng-Robinson EoS implying the Wong-Sandler mixing rule could be utilized as the most dependable thermodynamic model to study the thermodynamic consistency test of experimental vapor-liquid equilibrium (*VLE*) data.

In this theoretical research, we have investigated the thermodynamic consistency test of ten binary mixtures including Carbon dioxide (CO<sub>2</sub>) + ionic liquids. Experimental solubility data of binary mixtures have been taken out from literature. Pure component properties such as critical pressure (*P<sub>c</sub>*), critical temperature (*T<sub>c</sub>*) and etc. have been calculated using groups of contribution methods [13,14]. The total number of isotherms, studied in this paper are 28 that contains 280 data points. The applied thermodynamic model is the generic van der Waals (GvdW) equation of state coupled with modified van der Waals-Berthelot mixing rule [15].

## Modeling

The GvdW equation of state can be represented as follows [16]:

$$P = \frac{RT}{V - b} - \frac{a(T)}{V^2} \quad (1)$$

where *P* is known as the absolute pressure, *T* is the temperature, *R* is universal gas constant. *a*(*T*) and *b* can be determined as below:

$$a(T) = 0.421875 \frac{RT_c^2}{P_c} \alpha(T) \quad (2)$$

$$b = 0.175 \frac{RT_c}{P_c} \quad (3)$$

$$\alpha = \sum_{k=0}^{\leq 3} \beta_k \left( \frac{1}{T_r} - T_r \right), \quad \left( T_r \equiv \frac{T}{T_c} \right) \quad (4)$$

where  $T_c$  is critical Temperature,  $P_c$  is critical pressure and  $\beta_k$  is the adjustable parameter for each pure substance.

Parameters a and b which are intended for binary mixtures have been modeled and represented as below:

$$a = \sum_{i,j=1}^N \sqrt{a_i a_j} f_{ij}(T) (1 - k_{ij}) x_i x_j, \quad a_i = a_c \frac{R^2 T_{ci}^2}{P_{ci}} \alpha_i(T) \quad (5)$$

$$f_{ij}(T) = 1 + \tau_{ij}/T, \quad \text{Where,} \quad \tau_{ij} = \tau_{ji}, \quad \tau_{ii} = 0, \quad (6)$$

$$k_{ij} = \frac{l_{ij} l_{ji} (x_i + x_j)}{l_{ji} x_i + l_{ij} x_j}, \quad \text{Where,} \quad k_{ii} = 0 \quad (7)$$

$$b = \frac{1}{2} \sum_{i,j=1}^N (b_i + b_j) (1 - k_{ij}) (1 - m_{ij}) x_i x_j, \quad b_i = b_c \frac{RT_{ci}}{P_{ci}} \quad (8)$$

where  $m_{ij} = m_{ji}$ , and  $m_{ii} = 0$ .  $T_{ci}$  is the absolute critical temperature of  $i$ th species;  $P_{ci}$  is absolute critical pressure of the  $i$ th species;  $x_i$  is the mole fraction of the  $i$ th species.

Specification of the fugacity coefficient value of each species is absolutely important to calculate the phase equilibrium. Fugacity coefficient of  $i$ th species ( $\phi_i$ ) could be derived from the basic thermodynamic relation as follows [17]:

$$\ln \phi_i = \int_V^\infty \left\{ \left( \frac{\partial(nZ)}{\partial n_i} \right)_{T,V,n_j} - 1 \right\} \frac{dv}{v} - \ln Z \quad (9)$$

where  $Z$  is introduced as the compressibility factor. Fugacity coefficient of  $i$ th species for the represented equation of state is simplified as follows:

$$\ln \phi_i = \ln \frac{RT}{P(V-b)} + \frac{b'_i}{V-b} - \frac{a'_i + a}{VRT} \quad (10)$$

where  $a'_i$  and  $b'_i$  are given in the form below:

$$a'_i = 2 \sum_{j=1}^N \sqrt{a_i a_j} f_{ij} \left\{ 1 - k_{ij} - \frac{l_{ij} l_{ji} (l_{ij} - l_{ji}) x_i x_j}{(l_{ji} x_i + l_{ij} x_j)^2} \right\} - a \quad (11)$$

$$b'_i = \sum_{j=1}^N (b_i + b_j) (1 - m_{ij}) x_j \left\{ 1 - k_{ij} - \frac{l_{ij} l_{ji} (l_{ij} - l_{ji}) x_i x_j}{(l_{ji} x_i + l_{ij} x_j)^2} \right\} - b \quad (12)$$

The average relative deviation (ARD %), based on the pressure can be calculated as follows:

$$ARD\% = \frac{100}{N} \sum_{i=1}^N \left| \frac{P_i^{cal} - P_i^{exp}}{P_i^{exp}} \right| \quad (13)$$

## Thermodynamic Consistency Test

The Gibbs-Duhem fundamental equation for a binary system at an isotherm is known as below [16,18]:

$$\left[\frac{v^E}{RT}\right] dP = x_1 d(\ln \gamma_1) + x_2 d(\ln \gamma_2) \quad (14)$$

where  $v^E$  is determined as excess molar volume,  $T$  is absolute temperature,  $R$  is universal gas constant,  $x_1$  and  $x_2$  are mole fraction of components first and second in the liquid phase and also  $\gamma_1$  and  $\gamma_2$  are the activity coefficient of component 1 and 2. Eq. 14 can be rewritten as follows [19,20]:

$$\left[\frac{Z-1}{P}\right] dP = x_1 d(\ln \phi_1) + x_2 d(\ln \phi_2) \quad (15)$$

where  $Z$  is the compressibility factor,  $P$  is absolute pressure and  $\phi_1$  and  $\phi_2$  are the fugacity coefficients of ionic liquid as the solvent and dissolved refrigerant gas in the liquid phase.

The integral form of Eq. 15 can be expressed as follows:

$$\int \frac{1}{Px_2} dP = \int \frac{1}{(Z-1)\phi_2} d\phi_2 + \int \frac{1-x_2}{x_2(Z-1)\phi_1} d\phi_1 \quad (16)$$

In the above equation,  $\phi_1$ ,  $\phi_2$  and  $Z$  must be taken from thermodynamic modeling. In the Eq. 16, the left-hand side is labeled by  $A_p$  and the right-hand side by  $A_\phi$  which can be written as follows:

$$A_p = \int \frac{1}{Px_2} dP \quad (17)$$

$$A_{\phi_1} = \int \frac{1-x_2}{x_2(Z-1)\phi_1} d\phi_1 \quad (18)$$

$$A_{\phi_2} = \int \frac{1}{(Z-1)\phi_2} d\phi_2 \quad (19)$$

$$A_\phi = A_{\phi_1} + A_{\phi_2} \quad (20)$$

$$\int \frac{1}{Px_2} dP = \int \frac{1-x_2}{x_2(Z-1)\phi_1} d\phi_1 + \int \frac{1}{(Z-1)\phi_2} d\phi_2 \quad (21)$$

The equality between  $A_p$  and  $A_\phi$  with acceptable deviation proves the thermodynamic consistency for a set of data.

Average percent area deviation can be known as:

$$|\% \Delta A_i| = \left| \left\{ \frac{A_\phi - A_p}{A_p} \right\}_i \right| * 100 \quad (22)$$

Calculation of  $A_p$  for the liquid phase requires experimental  $P$ - $x$  data whereas with the aim of evaluating  $A_\phi$  for the liquid phase, fugacity coefficient of each species and compressibility factor are the requirement. It is significant to mention that for  $N$  number of experimental data point of each isotherm there are  $(N-1)A_p$  areas and  $(N-1)A_\phi$  areas for each binary system [21].

In order to determine thermodynamic consistency criteria, the first condition is to check the correlation between the experimental data and the thermodynamic model with a suitable

deviation of pressure. The model is accepted only if the average relative deviation, expressed as Eq. 14, is less than 10 percent. The second requirement is to check whether experimental data are able to satisfy the Gibbs-Duhem equation or not.

Each set of data can be in three statuses as follows:

- (1) If the total number of data points pass the area test, then the entire set of data is confirmed as Thermodynamically Consistent (TC).
- (2) If up to 25% of all points couldn't pass the area test but the rest of the data points pass the consistency test, then the whole set of data will be determined as Not Fully Consistent (NFC).
- (3) If further than 25% of data points could not pass the area test, then the whole set of data will be declared as Thermodynamically Inconsistent (TI).

## Data Selection And Modeling Parameters

This paper considers 10 binary CO<sub>2</sub> + ionic liquids mixtures which contains 28 isotherms with an overall number of 280 data points. Table 1 presents Molar Mass, critical temperature ( $T_c$ ), critical pressure ( $P_c$ ) and Parameters of the present equation of state for pure components. Table 2 demonstrates the experimental data studied in this paper with ranges of pressure and mole fraction for each isotherm.

## Result and discussion

Table 3 presents the optimal binary interaction parameter of the presented EoS along with average relative deviations ( $ARD\%$ ) and maximum relative deviations ( $MRD\%$ ). As shown in Table 3, the average relative deviation of each binary mixture is less than 10 percent which concluded that the first condition of the thermodynamic consistency test is satisfied.

**Table 1.** Pure compound properties Used in the Present EoS Model

Pure component	Molar Mass	$T_c$ (k)	$P_c$ (MPa)	$\beta_0$	$\beta_1$	$\beta_2$	$\beta_3$
CO <sub>2</sub>	60.075	378.77	6.37	1.0004	0.45587	-0.1130	0.06323
[pmpy][TF <sub>2</sub> N]	416.36	1234.2	2.755	1	0.0575	0	0
[Emim][LACTATE]	200.23	912.7	2.824	1	1.0735	0	0
[(CH <sub>2</sub> ) <sub>4</sub> SO <sub>3</sub> Hmim][TF <sub>2</sub> N]	499.43	1612.8	3.27	1	0.0461	0	0
[(CH <sub>2</sub> ) <sub>4</sub> SO <sub>3</sub> Hmim][HSO <sub>4</sub> ]	316.4	1433	2.588	1	0.7458	0	0
[EMMP][TF <sub>2</sub> N]	396.37	1038.7	2.588	1	0.3968	0	0
[TCD][TF <sub>2</sub> N]	532.56	1255.7	1.803	1	0.9674	0	0
[TDC][DCN]	318.5	1073.7	1.615	1	0.6254	0	0
[P <sub>4441</sub> ][TF <sub>2</sub> N]	497.5	1155	1.173	1	0.1458	0	0
[bmmim][TF <sub>2</sub> N]	433.4	1255.8	2.031	1	0.6936	0	0
[p(5)mppyrr][TF <sub>2</sub> N]	436.4	1221.9	1.828	1	0.7458	0	0

Table 4 represents the thermodynamic consistency test result for binary mixtures. As it is obvious in Table 4, the average area deviation ( $|\%A_{ave}|$ ), maximum area deviation ( $|\%A_{max}|$ ), number of data points ( $N_D$ ) and the result of the thermodynamic consistency test are presented for each isotherm.

As it is obvious in Table 4, among the total number of isotherms, used in this paper, 10 cases of all are declared to be thermodynamically consistent (TC) with area deviations within the recognized limits, 14 isotherms of this paper are considered to be not fully consistent (NFC) which means less than 25 percent of data points have exceeded the limits and just 4 isotherms are claimed to be thermodynamically inconsistent (TI) which declares that more than 25 percent of data points of each isotherm has exceeded the established limit of area deviations.

**Table 2.** Details on phase equilibrium data of 10 binary systems

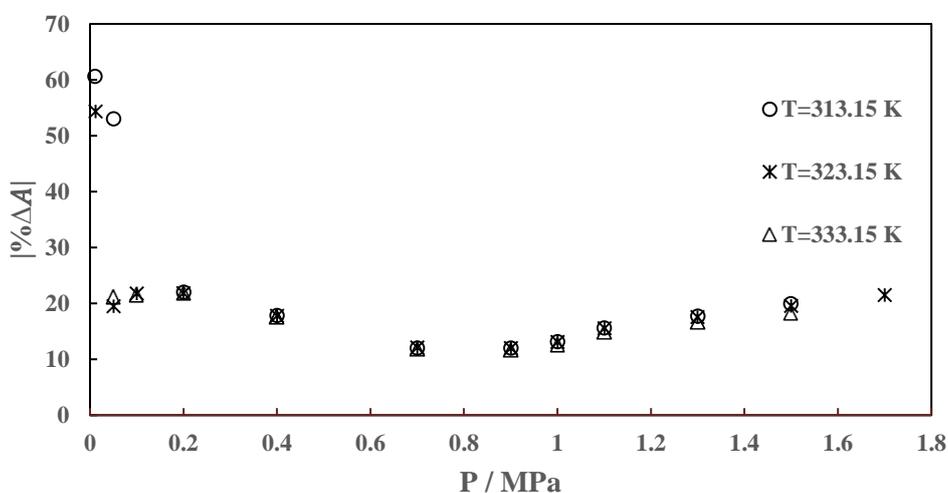
System (1)/(2)	T (k)	Range of data		Reference
		Range of $x_1 * 100$	Range of $P$ (MPa)	
CO <sub>2</sub> /[(CH <sub>2</sub> ) <sub>4</sub> SO <sub>3</sub> Hmim][HSO <sub>4</sub> ]	313.15	0.175 - 5.520	0.0498 - 1.2997	[22]
	323.15	3.190 - 6.140	0.9001 - 1.7000	[22]
CO <sub>2</sub> /[(CH <sub>2</sub> ) <sub>4</sub> SO <sub>3</sub> Hmim][TF <sub>2</sub> N]	313.15	0.133 - 25.80	0.0098 - 1.9000	[22]
	323.15	0.158 - 18.25	0.0098 - 1.5002	[22]
CO <sub>2</sub> /[bmmim][TF <sub>2</sub> N]	298.15	1.400 - 38.20	0.0500 - 1.8997	[23]
	313.15	1.100 - 31.10	0.0500 - 1.8997	[23]
	343.15	6.000 - 21.10	0.0501 - 1.8997	[23]
CO <sub>2</sub> /[Emim][LACTATE]	313.15	15.20 - 24.20	0.3999 - 1.2997	[22]
	323.15	7.140 - 19.10	0.0999 - 0.9998	[22]
	333.15	4.300 - 16.70	0.0500 - 0.9998	[22]
CO <sub>2</sub> /[EMMP][TF <sub>2</sub> N]	313.15	1.600 - 31.65	0.0098 - 1.9000	[24]
	323.15	0.209 - 26.73	0.0100 - 1.8996	[24]
	333.15	0.182 - 16.83	0.0101 - 1.2998	[24]
CO <sub>2</sub> /[p(5)mpyr][TF <sub>2</sub> N]	298.15	0.3 - 40.6	0.0097 - 1.8998	[23]
	313.15	0.3 - 33.3	0.0097 - 1.9002	[23]
	343.15	0.7 - 21.8	0.0500 - 1.8994	[23]
CO <sub>2</sub> /[P <sub>4441</sub> ][TF <sub>2</sub> N]	298.15	0.300 - 39.30	0.0099 - 1.8999	[23]
	313.15	1.200 - 32.60	0.0498 - 1.8995	[23]
	343.15	0.700 - 23.00	0.0510 - 1.8997	[23]
CO <sub>2</sub> /[Pmpy ][TF <sub>2</sub> N]	313.15	1.090 - 31.70	0.0500 - 1.8997	[22]
	323.15	0.928 - 27.60	0.0500 - 1.9008	[22]
	333.15	0.219 - 23.20	0.0100 - 1.8996	[22]
CO <sub>2</sub> /[TCD][TF <sub>2</sub> N]	313.15	1.300 - 33.27	0.0499 - 1.6997	[24]
	323.15	1.052 - 31.27	0.0501 - 1.8998	[24]
	333.15	0.230 - 28.17	0.0101 - 1.8998	[24]
CO <sub>2</sub> /[TDC][DCN]	313.15	0.178 - 24.79	0.0101 - 1.7001	[24]
	323.15	0.187 - 24.03	0.0118 - 1.9006	[24]

**Table 3.** Binary Interaction Parameters, ARD% and MRD% of binary mixtures

System (1)/(2)	T (k)	$l_{12}$	$l_{21}$	$\tau_{12}$	$m_{12}$	ARD%	MRD%
CO <sub>2</sub> /[(CH <sub>2</sub> ) <sub>4</sub> SO <sub>3</sub> Hmim][HSO <sub>4</sub> ]	313.15	0.3496	0.8196	16.7411	-0.1697	3.8047	5.7098
	323.15	0.4118	0.4604	1.4523	-0.7395	2.0211	2.222
CO <sub>2</sub> /[(CH <sub>2</sub> ) <sub>4</sub> SO <sub>3</sub> Hmim][TF <sub>2</sub> N]	313.15	0.4042	0.501	2.444	-0.6596	0.8863	2.6094
	323.15	0.4033	0.4868	2.5648	-0.5525	1.5393	4.7548
CO <sub>2</sub> /[bmmim][TF <sub>2</sub> N]	298.15	0.4887	0.4905	134.1301	-0.4952	0.8816	2.453
	313.15	0.4866	0.4875	134.3856	-0.5900	0.7945	4.0011
	343.15	0.4899	0.4771	137.0478	-0.6841	3.6486	18.4883
CO <sub>2</sub> /[Emim][LACTATE]	313.15	0.2371	0.2729	132.0284	-0.3282	0.0455	0.1137
	323.15	0.366	0.1873	136.2312	-0.3198	0.4319	1.2214
	333.15	0.3581	0.1745	133.5198	-0.3178	0.0482	0.3651
CO <sub>2</sub> /[EMMP][TF <sub>2</sub> N]	313.15	0.3874	0.3649	210.1831	-0.6049	1.1235	6.1456
	323.15	0.3818	0.3761	210.0378	-0.5984	1.3907	2.1536
	333.15	0.3855	0.3701	211.4935	-0.6044	1.238	5.3487
CO <sub>2</sub> /[p(5)mpyr][TF <sub>2</sub> N]	298.15	0.3838	0.3871	174.3809	-0.603	0.6752	2.5856
	313.15	0.3984	0.4042	192.1659	-0.6382	0.5993	2.5797
	343.15	0.4088	0.4281	148.9627	-0.6348	1.7536	7.9747
CO <sub>2</sub> /[P <sub>4441</sub> ][TF <sub>2</sub> N]	298.15	0.4201	0.418	175.8401	-0.6931	0.6662	2.018
	313.15	0.4163	0.4119	174.5696	-0.6821	1.3874	7.483
	343.15	0.3985	0.3809	192.8922	-0.6472	1.3236	5.1909
CO <sub>2</sub> /[Pmpy ][TF <sub>2</sub> N]	313.15	0.3951	0.3909	178.8986	-0.6213	0.8286	4.0152
	323.15	0.3992	0.3882	190.8733	-0.6339	0.9336	3.6189
	333.15	0.3999	0.3841	190.609	-0.6326	1.4724	8.7459
CO <sub>2</sub> /[TCD][TF <sub>2</sub> N]	313.15	0.4014	0.3826	196.4743	-0.6358	2.198	8.9265
	323.15	0.4122	0.4074	178.4359	-0.6525	1.4122	7.5445
	333.15	0.4026	0.3887	191.5622	-0.635	0.8528	6.3693
CO <sub>2</sub> /[TDC][DCN]	313.15	0.4075	0.3756	177.5013	-0.69	1.3492	6.138
	323.15	0.4083	0.3864	162.9881	-0.6845	1.1672	5.4088
	333.15	0.4083	0.3864	162.9881	-0.6845	1.2204	6.3603

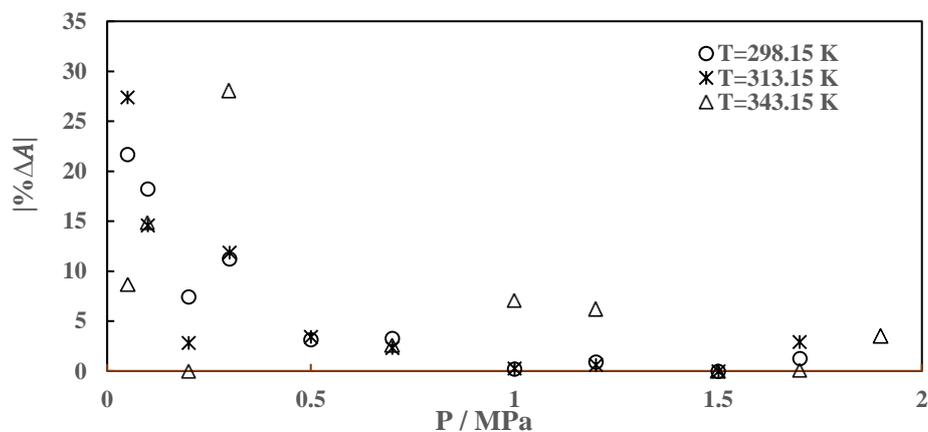
**Table 4.** Obtained result with average percent area deviation, maximum area deviation of CO<sub>2</sub> at all isotherms.

System (1) / (2)	T (k)	%A <sub>ave</sub>	%A <sub>max</sub>	N <sub>D</sub>	result
CO <sub>2</sub> /[(CH <sub>2</sub> ) <sub>4</sub> SO <sub>3</sub> Hmim][HSO <sub>4</sub> ]	313.15	45.2838	86.2924	4	TI
	323.15	13.5598	24.6564	6	NFC
CO <sub>2</sub> /[(CH <sub>2</sub> ) <sub>4</sub> SO <sub>3</sub> Hmim][TF <sub>2</sub> N]	313.15	25.8779	97.8815	7	TI
	323.15	26.386	71.8385	5	TI
CO <sub>2</sub> /[bmmim][TF <sub>2</sub> N]	298.15	9.2871	20.5026	11	NFC
	313.15	8.8745	23.1339	11	NFC
	343.15	7.2107	13.1904	11	TC
CO <sub>2</sub> /[Emim][LACTATE]	313.15	2.9471	5.3572	5	TC
	323.15	3.7464	29.8757	5	NFC
	333.15	4.9875	9.987	7	TC
CO <sub>2</sub> /[EMMP][TF <sub>2</sub> N]	313.15	7.2431	23.8386	10	NFC
	323.15	0.0117	0.0634	13	TC
	333.15	11.304	89.6658	10	NFC
CO <sub>2</sub> /[p(5)mpyrr][TF <sub>2</sub> N]	298.15	24.3932	61.9733	10	TI
	313.15	8.3983	19.4812	12	TC
	343.15	11.5305	30.7383	11	NFC
CO <sub>2</sub> /[P <sub>4441</sub> ][TF <sub>2</sub> N]	298.15	11.7108	61.4322	12	NFC
	313.15	6.029	27.3911	11	NFC
	343.15	6.5456	28.0367	11	NFC
CO <sub>2</sub> /[Pmpy ][TF <sub>2</sub> N]	313.15	7.7414	21.4867	12	NFC
	323.15	7.1634	19.3251	12	TC
	333.15	8.2305	19.7698	13	TC
CO <sub>2</sub> /[TCD][TF <sub>2</sub> N]	313.15	6.5426	21.5568	11	NFC
	323.15	7.3252	18.6595	12	TC
	333.15	5.7178	19.5502	13	TC
CO <sub>2</sub> /[TDC][DCN]	313.15	14.6685	61.3748	11	NFC
	323.15	13.7623	56.0489	13	NFC
	333.15	8.7959	18.0566	11	TC

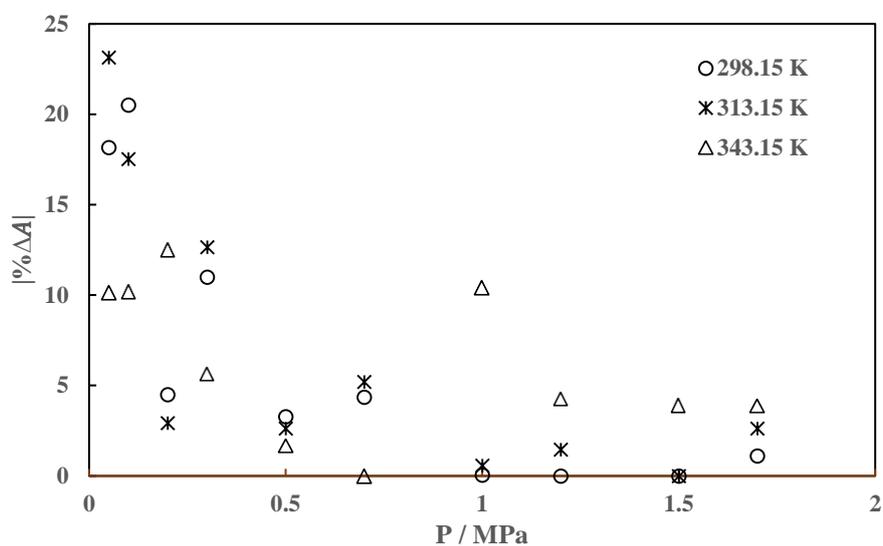
**Fig. 1.** Average percent area deviation for liquid phase of CO<sub>2</sub> + [TDC][DCN] in three different isotherms.

A graphical illustration of the results is shown in Figs. 1-4. Fig. 1 indicates the average percent area deviation of CO<sub>2</sub>/[TDC][DCN] at three different Temperatures which declares not fully consistent at 313.15 K with two points higher than 20%, not fully consistent at 323.15 K with 1 point exceeded the limit and thermodynamically consistent at 333.15 K. Fig. 2 shows the average percent area deviation of CO<sub>2</sub> + [P<sub>4441</sub>][TF<sub>2</sub>N] in 298.15 K, 313.15 K and 343.15 K that declares to be not fully consistent in all isotherms. Fig. 3 shows average percent area deviation of CO<sub>2</sub> / [bmmim][TF<sub>2</sub>N] in 298.15 K, 313.15 K, 343.15 K which represents to be not fully consistent at 298.15 K with one point exceeded the limit, not fully consistent at 313.15 K with one point higher 20 % area deviation and thermodynamically consistent at 343.15 K. Fig. 4 shows average percent

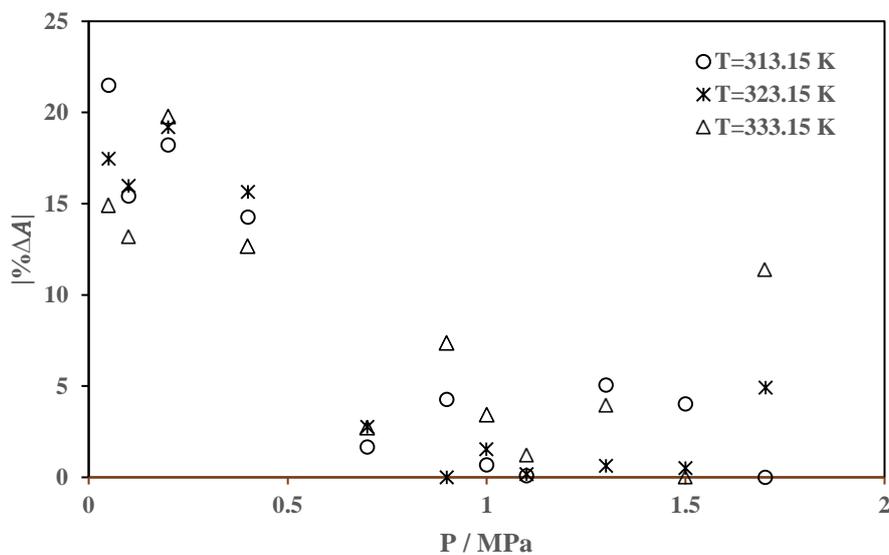
area deviations of  $\text{CO}_2/[\text{Pmpy}][\text{TF}_2\text{N}]$  in 313.15 K, 323.15 K and 333.15 K that declares to be thermodynamically consistent at 313.15 K with one point exceeded the limit and thermodynamically consistent at 323.15 K and 333.15 K.



**Fig. 2.** Average percent area deviation for liquid phase of  $\text{CO}_2 + [\text{P}_{4441}][\text{TF}_2\text{N}]$  in three different isotherms



**Fig. 3.** Average percent area deviation for liquid phase of  $\text{CO}_2 + [\text{bmmim}][\text{TF}_2\text{N}]$  in three different isotherms.



**Fig. 4.** Average Percent Area deviation for liquid phase of  $\text{CO}_2 + [\text{Pmpy}][\text{TF}_2\text{N}]$  in three different isotherms

## Conclusion

In this paper, the thermodynamic consistency test of 10 binary systems including carbon dioxide along with room temperature ionic liquids using Generic van der Waals EoS coupled with van der Waals-Berthelot mixing rule was studied. The result of modeling the experimental *VLE* data illustrates the capability of present EoS. The proposed method of the thermodynamic consistency test is able to give an acceptable result about the consistency or inconsistency of experimental *P-x* data of binary mixtures. In addition, it shall be illustrated that systems with lower *ARD%* error are more trustable which means that the accuracy of experimental *P-x* data can be obtained whenever the first condition is comprehensively fulfilled.

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