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Saturated Virial Coefficient of the Environmentally Friendly Refrigerant Fluids: R365mfc and R152a

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Abstract- This work presents the saturated second Virial coefficient of new environmentally friendly refrigerants 1,1-difluoroethane (R152a), 1,1,1,3,3-Pentafluorobutane (R365mfc) and their mixture. The vapor phase behavior of the mixture was investigated using the Virial equation of state combined with group contribution method of modified UNIFAC. The work has enabled a highly accurate predicted saturated second Virial coefficient data as function of composition in a temperature range of $T=260\text{K}$ to $T=380\text{K}$. The Tsonopoulos second Virial coefficient model has been investigated and compared with experimental data of McLinden et.al from National Institute of Standard and Technology (NIST). The results yielded a maximum deviation of 4.06%, in a temperature range of $T=298\text{--}300\text{K}$, whereas, for a temperature range of $T=323\text{--}325\text{K}$ a maximum deviation less than 2.59% was recognized for R365mfc. A negative deviation less than 12.3% was achieved for R152a.

Keywords- R152a, R365mfc, Virial coefficient, Unifac, Tsonopoulos, McLinden.

I. INTRODUCTION

The last two decades have witnessed a significant increase of the harmful materials of Chlorofluorocarbons (CFCs) and Hydrochlorofluorocarbons (HCFCs) based refrigerants in the atmosphere. These materials have been widely used as solvents, foam blowing agents, aerosols and especially as refrigerants due to their preeminent properties such as stability, non-toxicity, non-flammability and availability. However, these substances have a harmful effect on the earth's protective ozone layer. Since the declaration of the Montreal protocol in 1987 the use of these substances is consequently regulated [1]. Moreover the CFCs had been detected as substances contributing to global warming. Nowadays the world leading countries have legalized to stop the consumption of CFCs by replacing them with HFCs [3-5].

This paper supports more accurate data of the saturated second Virial coefficient, as a necessary parameter in molecular thermodynamics, including the pure fluids and mixtures of R152a and R365mfc. This parameter could enable better understanding of the fluid phase behavior for this mixture. The R152a is a HFC type refrigerant. This fluid has zero ODP and a GWP value of 120. The boiling point temperature at a pressure of $p=1.013\text{ bar}$ is $T_b=-24.0^\circ\text{C}$, the molecular weight $M=66.1\text{ kg/kmol}$. R152a is a medium pressure refrigerant for the medium temperature refrigeration range [2]. The physical, thermodynamic and refrigeration characteristics are similar to those of the refrigerants R12 and R134a. Although R152a is a good refrigerant substitute for R12, it is not used in its pure form because of its flammability (flammability limits 3.7–21.8% by volume in air). For this reason, R152a is labeled as "highly flammable". The R365mfc is a HFC type refrigerant. This fluid has zero ODP and a GWP value of 782. The boiling point temperature at a pressure $p=1.013\text{ bar}$ is $T_b=+41.4^\circ\text{C}$, the molecular weight is $M=148.07\text{ kg/kmol}$. R365mfc is a new fluid which is mainly used for the production of rigid polyurethane foams used in insulation purposes where a liquid foaming agent with a low thermal conductivity and a high vapor pressure at low temperatures are needed. Regarding to thermodynamic properties and safety requirements, R365mfc is employed as a main component in binary blends with 7 or 13 mass% with 1,1,1,2,3,3,3-Heptafluoropropane (R227ea) in the production of liquid foaming agents [2]. Besides the fact that this fluid has no negative impact on the ozone layer, further environmental benefits can be achieved using R365mfc, like in the production of polyurethane foams. To the best of our knowledge, only a very limited amount of data for the Virial coefficient particularly at saturation conditions are available in the literature for R365mfc and R152a.

II. PREDICTIVE MODELS

Beside the previous equations; the Virial equation of state was also used to predict the density of the vapor phase. The main advantage of this equation is its rigorous theoretical background to describe the behavior of mixtures, as the Virial coefficients can be connected to the potential functions of the intermolecular forces and has been widely used in statistical thermodynamics. The

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main disadvantage of this equation is its validity only for gases with low or moderate densities. Most commonly used in the power series expansion in volume for the compressibility factor:

$$Z = \frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2} + \dots \quad (1)$$

The lack of the information of the third Virial coefficient leads to the situation that this equation is written in one parameter form; whereas hardly any data are available for the third coefficient [6].

$$Z = 1 + \frac{BP}{RT} \quad (2)$$

Smith et al [7] recommended the use of the two parameter Virial EOS up to pressures of 15 bar and the three parameter form up to 50 bar. The extension of the Virial EOS to mixtures is a rigorous process and is based on theoretical rather than empirical grounds. The interaction between the gases are incorporated in the two parameter Virial EOS as the mixture second Virial coefficient, which is related to the pure component and cross second Virial coefficient for a binary systems using the quadratic mixing rule [8]:

$$B_{\text{mix}} = \sum_{i=1}^2 \sum_{j=1}^2 y_i y_j B_{ij} \quad (3)$$

Many second Virial coefficients which have been determined from experimental data are collected by Dymond and Smith [9] and also stored in the data banks like DDB [17]. In this work the method of Tsonopoulos [10] was used, which delivered good results for the prediction of this coefficient. The acentric factor, critical temperature and pressure for mixture were predicted according to Kay's rule [11]. In this method the parameter B can be expressed as:

$$\frac{BP_c}{RT_c} = b^{(0)}(T_r) + \omega b^{(1)}(T_r) \quad (4)$$

Where T_r , ω are the reduced temperature and acentric factor respectively. For the mixture the linear mixing rules for both values were used. The empirical correlations for $b^{(0)}(T_r)$ and $b^{(1)}(T_r)$ are given by:

$$b^{(0)}(T_r) = 0.1445 - \frac{0.330}{T_r} - \frac{0.1385}{T_r^2} - \frac{0.0121}{T_r^3} - \frac{0.000607}{T_r^8} \quad (5)$$

$$b^{(1)}(T_r) = 0.0637 + \frac{0.331}{T_r^2} - \frac{0.423}{T_r^3} - \frac{0.008}{T_r^8} \quad (6)$$

The vapor density predicted by Virial EOS was estimated from the Leiden form [6]:

$$\rho^v = \left[\frac{RT}{P} + B_{\text{mix}} \right]^{-1} \quad (7)$$

Table I. Properties of the fluids.

Component	M_w (kg/kmol)	T_c (K)	P_c (bar)	ρ_c (kg/m ³)	ω
R365mfc	148.07	460.0	3266.0	473.84	0.377
R152a	66.051	386.41	4516.8	368.0	0.27521

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In this method the temperature independent combinatorial part takes into account the size and the form of the molecules, which considers the entropic contribution and the residual part, considers the enthalpic interactions as follows:

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \quad (8)$$

The combinatorial part $\ln \gamma_i^C$ can be calculated using the following equation, which is identical to the UNIQUAC model:

$$\ln \gamma_i^C = 1 - V_i + \ln V_i - 5q_i \left(1 - \frac{V_i}{F_i} + \ln \frac{V_i}{F_i} \right) \quad (9)$$

Where V_i (Volume/mole fraction ratio) and F_i (surface area/mole fraction ratio) can be calculated for a given composition using the relative van der Waals volume r_i and van der Waals surface areas q_i of the molecules.

$$V_i = \frac{r_i}{\sum_j r_j x_j} \quad F_i = \frac{q_i}{\sum_j q_j x_j} \quad (10)$$

The relative van der Waals properties r_i and q_i can be obtained using the relative van der Waals group volumes R_k and relative van der Waals group surface areas Q_k , which can be derived from x-ray data. Tabulated values for R_k and Q_k can be found in Hansen et al. [12]. They can also be derived from the tabulated van der Waals properties published by Bondi [13].

$$r_i = \sum_k v_k^{(i)} R_k \quad q_i = \sum_k v_k^{(i)} Q_k \quad (11)$$

where $v_k^{(i)}$ is the number of functional groups of type k in compound i . The temperature dependent residual part $\ln \gamma_i^R$ takes into account the interactions between the different compounds. In group contribution methods, this part is calculated by the solution of groups concept using group activity coefficients Γ_k and $\Gamma_k^{(i)}$:

$$\ln \gamma_i^R = \sum_k v_k^{(i)} (\ln \Gamma_k - \ln \Gamma_k^{(i)}) \quad (12)$$

Γ_k and $\Gamma_k^{(i)}$ are the group activity coefficients for group k in the mixture, for the pure compound i . The UNIQUAC equation is used to describe the mole fraction dependence of the group activity coefficients as follows:

$$\ln \Gamma_k = Q_k \left[1 - \ln \left(\sum_m \Theta_m \Psi_{mk} \right) - \sum_m \frac{\Theta_m \Psi_{km}}{\sum_n \Theta_n \Psi_{nm}} \right] \quad (13)$$

The surface area fractions Θ_m and the group mole fractions X_m of group m can be calculated using the following relations:

$$\Theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n} \quad X_m = \frac{\sum_j v_m^{(j)} x_j}{\sum_j \sum_n v_n^{(j)} x_j} \quad (14)$$

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The parameter Ψ_{nm} contains the group interaction parameter a_{nm} between the functional groups n and m which is described as follows:

$$\Psi_{nm} = \exp\left(-\frac{a_{nm}}{T}\right) \quad (15)$$

For every main group combination two temperature independent group interaction parameters

(a_{nn}, a_{mm}) are required, the group interaction parameters between identical main groups (a_{nn}, a_{mm}) are equal to zero. The modification of the modified UNIFAC compared to the original UNIFAC was established firstly by Kikic et al. [14]. The combinatorial part is calculated using the following slightly modified empirical equation:

$$\ln \gamma_i^c = 1 - V_i' + \ln V_i' - 5q_i \left(1 - \frac{V_i}{F_i} + \ln \frac{V_i}{F_i}\right). \quad (16)$$

For which V_i is:

$$V_i' = \frac{r_i^{2/3}}{\sum_j r_j^{2/3} x_j}. \quad (17)$$

III. RESULTS AND DISCUSSIONS

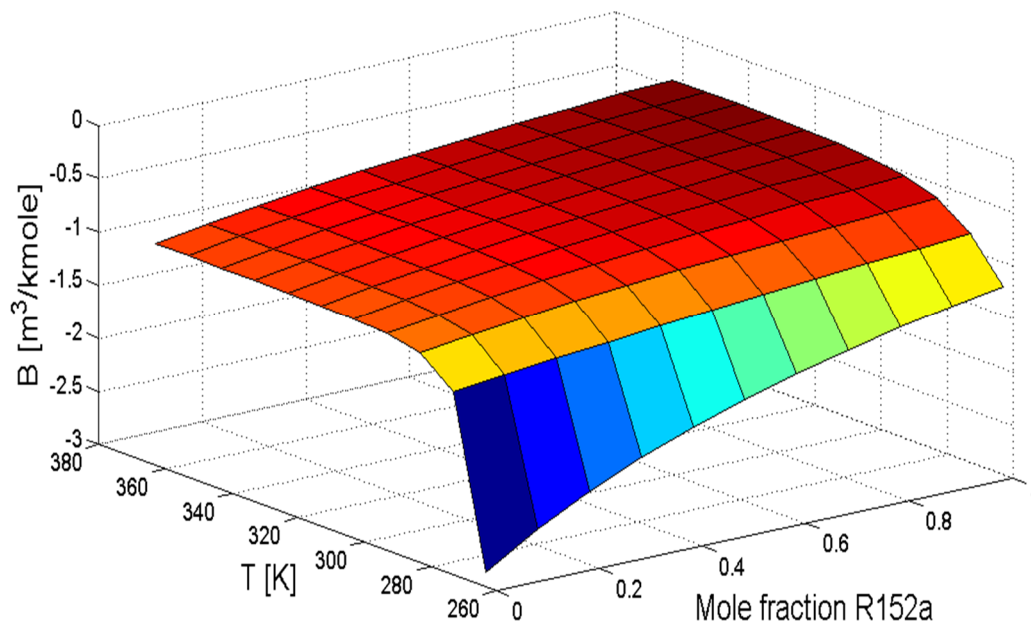


Fig.1. Temperature and composition dependent of the second virial coefficient of the system R152a (1) and R365mfc (2).

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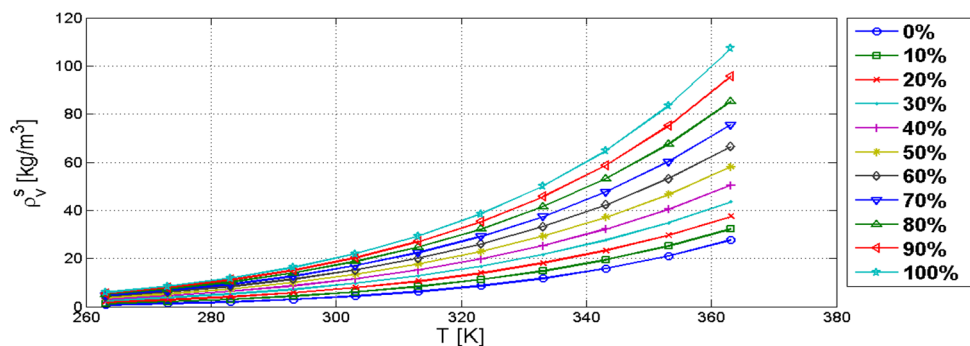


Fig.2. Saturated vapor density varying with temperature of the system R152a and R365mfc from modified UNIFAC-Virial equation.

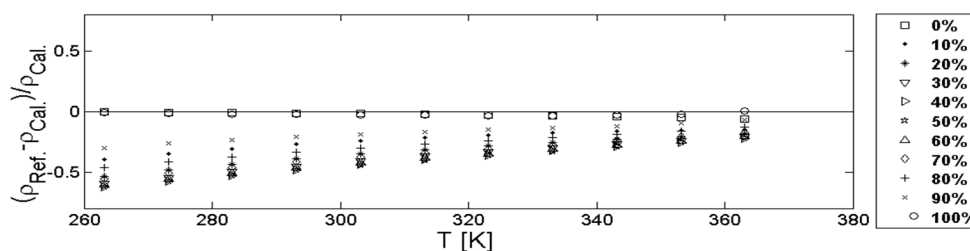


Fig.3. Relative deviation in saturated vapor density data for the system R152a and R365mfc from modified UNIFAC-Virial equation.

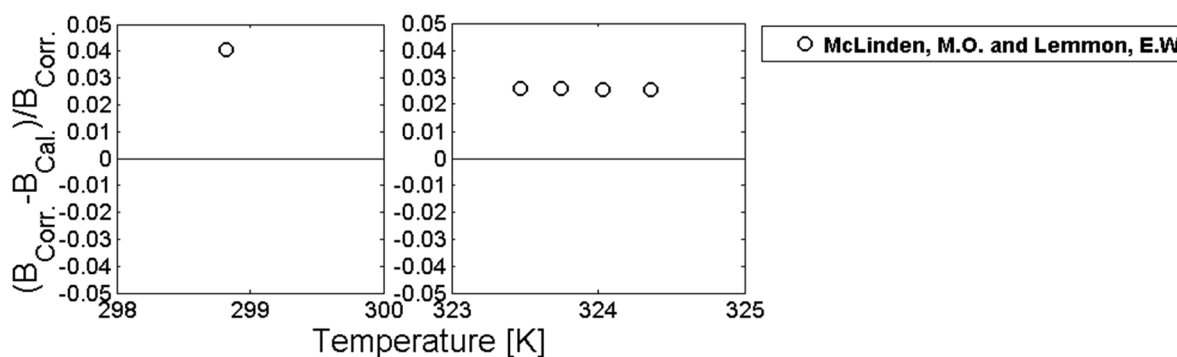


Fig.4. Relative deviation between our calculated and literature data of the second virial coefficient of R365mfc.

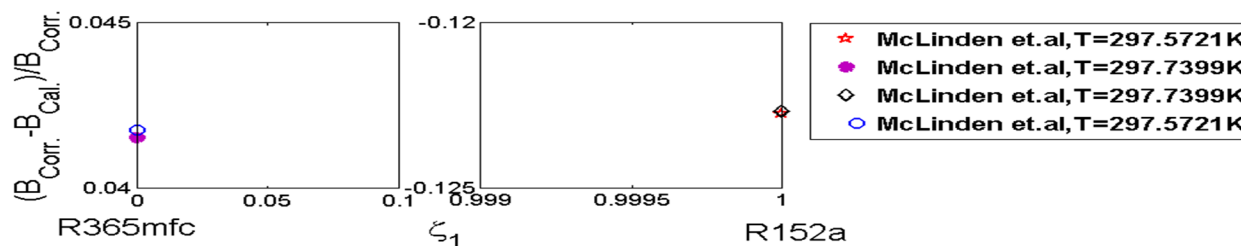


Fig.5. Relative deviation between our calculated and literature data of the second virial coefficient of R152a and R365mfc.

As is seen in Fig.1, the virial coefficients are composition and temperature dependent. The relation shows that the increase in the

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temperature will lead to increase the value of this parameter. At low temperature, the second virial coefficient is an always negative value, which indicates that the molar volume of the real gas is smaller than the corresponding molar volume of the ideal gas due to attractive interactions. Fig.2 illustrated the variation of vapor density with temperature predicted by virial equation. Fig.3. presented the relative deviation in saturated vapor density data for this system predicted by modified UNIFAC-Virial model, a maximum deviations reached on the way of increasing the composition of the high component R365mfc. Fig.4 explains the variation of the temperature and relative deviation to experimental data in second virial coefficient of pure R365mfc. As seen, the measurement was conducted in a saturation temperature range of $T=298-325\text{K}$ and pressure range of $p=0.58-1.44\text{bar}$. The data of McLinden et al. [15][16] has been investigated and compared with Tsonopoulos [10] model. This model yielded a maximum deviation of 4.06%, in a temperature range of $T=298-300\text{K}$. Whereas, for a temperature range of $T=323-325\text{K}$ a maximum deviation less than 2.59% was recognized. Meanwhile, Fig.5 describes the same results executed for both pure fluids at temperature of $T=297.5721\text{K}$, 297.7399K , and a pressure of $p=4.76\text{bar}$, 4.19bar . The data of McLinden et al. [15] has reached a maximum deviation less than 4% in case of R365mfc, however a negative deviation less than 12.3% was achieved for R152a. Unfortunately, this model has failed to deliver satisfied results for mixture data.

IV. CONCLUSIONS

The work has delivered important thermodynamic data of the vapor density and second virial coefficient of the environmentally friendly system of R152a and R365mfc. The vapor phase behavior of the mixture was investigated using the Virial equation of state combined with group contribution method of modified UNIFAC. The Virial-Unifac model was chosen, since it is needed for providing reliable results for new refrigerants as well as a large range of applicability in the vapor phase. The second Virial coefficients by these models were compared with data obtained by the high precision fundamental equations of state by McLinden et.al from National Institute of Standard and Technology (NIST). The simulation results achieved good agreement with this model, particularly for the pure fluids.

V. ACKNOWLEDGMENTS

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Nomenclature

CFCs	chlorofluorocarbons
HCFCs	hydrochlorofluorocarbons
HFCs	hydrofluorocarbons
EOS	equation of state
GWP	global warming potential
ODP	ozone depletion potential
DDB	dortmund data bank
UNIFAC	universal quasi chemical functional group activity
NIST	national institute of standard and technology
T_c, P_c	critical temperature and pressure
T_r	reduced temperature
g^E	excess Gibbs energy
r_i	relative van der Waals volume of component i
x_i	mole fraction of component i in the liquid phase
q_i	relative van der Waals surface area of component i
$\Gamma_k^{(i)}$	group activity coefficient of group k in pure component i.

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Γ_k group activity coefficient of group k in the mixture.

$v_k^{(i)}$ number of groups k in component i.

$v^{(i)}$ number of groups in component i.

$n^{(i)}$ number of moles of component i.

$\sum_i n^{(i)} v^{(i)}$ total number of moles of groups in the mixture.

$X_k^{(i)} = \frac{v_k^{(i)}}{v^{(i)}}$ group mole fraction of group k in compound i.

$X_k = \frac{\sum_i n^{(i)} v_k^{(i)}}{\sum_i n^{(i)} v^{(i)}}$ group mole fraction of group k in the mixture.

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