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Excess Gibbs Energy and Saturation Pressure of the Environmentally Friendly Refrigerant Mixture: R365mfc and R152a

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Abstract- This work presents the saturation pressure of new environmentally friendly refrigerants 1,1-difluoroethane (R152a) and 1,1,1,3,3-Pentafluorbutane (R365mfc), beside their mixture. Special attention was given to enable a highly accurate predicted saturation pressure and excess Gibbs energy data as function of composition in a temperature range of T=260K to T=380K, for the pure fluid and the mixture. The simulation data for the saturation pressure were obtained using the modified Unifac method, Lee Kesler and Hoffman Florin models and validated with the high precision fundamental equations of state by Outcalt and McLinden from National Institute of Standard and Technology (NIST). Among all the model of Lee and Kesler have shown good results for fitting the light component R152a, maximum positive deviation less than 1% was reached. Whereas the model of Hoffman Florin yielded good results for R365mfc, maximum positive deviation less than 2.85% was reached. The excess Gibbs energy function for the mixture was realized in a temperature range of T=260K to T=380K by the modified UNIFAC method.

Keywords- R152a, R365mfc, Excess Gibbs Energy, Lee Kesler, Hoffman Florin, Unifac.

I. INTRODUCTION

Since the declaration of the Montreal protocol in 1987 the use of the harmful materials of Chlorofluorocarbons (CFCs) and Hydro-chlorofluorocarbons (HCFCs) based refrigerants in the atmosphere is consequently regulated [1]. 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. Moreover the CFCs had been recognized as materials contributing to the phenomena of the global warming. The international efforts have legalized to stop the consumption of CFCs by replacing them with new HFCs [3-5].

This paper supports most important thermodynamics data for those materials, including the pure fluids and mixtures of R152a and R365mfc. 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 bar is ϑ^s=–24.0°C, the molecular weight M=66.1 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 bar is ϑ^s=+41.4°C, the molecular weight is at M=148.07 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 excess Gibbs energy and saturated pressure of R365mfc and R152a are available in the literature.

II. PREDICTIVE MODELS

The equation type of Hoffman Florin (1), (2) respectively has been implemented to detect the saturation pressure . This equation based on the charts developed by Cox [6] and it has two adjustable parameters α and β. It is calculated as follows:

$$\ln\frac{P^S}{P_0} = \alpha + \beta * f(T) \tag{1}$$

$$f(T) = \frac{1}{T} - 7.9151*10^{-3} + 2.6726*10^{-3}*\log T - 0.8625*10^{-6}*T \tag{2}$$

The equation can be fitted to two or more known data points for the saturation pressure. The parameter α and β can then be calculated via:

$$\alpha = \ln\frac{P_1^S}{P_0} - \ln\frac{P_1^S}{P_2^S} * \frac{f(T_1)}{f(T_1) - f(T_2)} \tag{3}$$

$$\beta = \frac{\ln\frac{P_1^S}{P_2^S}}{f(T_1) - f(T_2)} \tag{4}$$

A more convenient equation of Lee and Kesler [10] was also used to estimate the saturation pressure as follows:

$$P^S = P_c \exp(A + wB) \tag{5}$$

In this equation A and B are functions on the critical temperature of the fluid.

In 1975, the UNIFAC group contribution method was published by Fredenslund et al. [7-10]. Like the ASOG method, the UNIFAC method is based on the solution of groups concept. However in the UNIFAC method, the activity coefficients are calculated from a combinatorial and a residual part exactly like in the UNIQUAC model. 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:

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

$$\ln\gamma_i = \ln\gamma_i^C + \ln\gamma_i^R \tag{6}$$

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

$$\ln\gamma_i^C = 1 - V_i + \ln V_i - 5q_i\left(1 - \frac{V_i}{F_i} + \ln\frac{V_i}{F_i}\right) \tag{7}$$

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.

$$V_i = \frac{r_i}{\sum_j r_j x_j} \tag{8}$$

$$F_i = \frac{q_i}{\sum_j q_j x_j} \tag{9}$$

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. [10].They can also be derived from the tabulated van der Waals properties published by Bondi [11].

$$r_i = \sum_k v_k^{(i)} R_k \tag{10}$$

$$q_i = \sum_k v_k^{(i)} Q_k \tag{11}$$

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 $\Gamma_k^{(i)}$ [6]:

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

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 [6]:

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

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

$$\Theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n} \tag{14}$$

$$X_m = \frac{\sum_j v_m^{(j)} x_j}{\sum_j \sum_n v_n^{(j)} x_j} \tag{15}$$

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

$$\Psi_{nm} = \exp\left(-\frac{a_{nm}}{T} \right) \tag{16}$$

For every main group combination two temperature independent group interaction parameters

(a_{nm}, a_{mn}) are required, the group interaction parameters between identical main groups (a_{nn}, a_{mm}) are equal to zero. All the parameters were fitted to consistent experimental vapor-liquid equilibrium data which are stored in the Dortmund Data Bank [12]. To improve and treat the weaknesses of UNIFAC, the modified UNIFAC method was developed [13].The main differences compared to original UNIFAC are [6]:

- An empirically modified combinatorial part was introduced to improve the results for asymmetric systems.
- Temperature dependent group interaction parameters are used.
- Additional main groups were added, for example for cyclic alkanes and formic acid.

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:

$$\ln \gamma_i^{C} = 1 - V_i' + \ln V_i' - 5q_i\left(1 - \frac{V_i}{F_i} + \ln\frac{V_i}{F_i}\right). \qquad (17)$$

For which V_i is:

$$V_i' = \frac{r_i^{2/3}}{\sum_j r_j^{2/3} x_j}. \qquad (18)$$

Weidlich [15-16] has recommended using the value 3/4 for the volume fraction exponential term as follows:

$$V_i' = \frac{r_i^{3/4}}{\sum_j r_j^{3/4} x_j}. \qquad (19)$$

To describe the temperature dependence, linear or quadratic temperature dependent parameters were introduced as follows:

$$\Psi_{nm} = \exp\left(-\frac{a_{nm} + b_{nm}T + c_{nm}T^2}{T}\right). \qquad (20)$$

III. RESULTS AND DISCUSSIONS

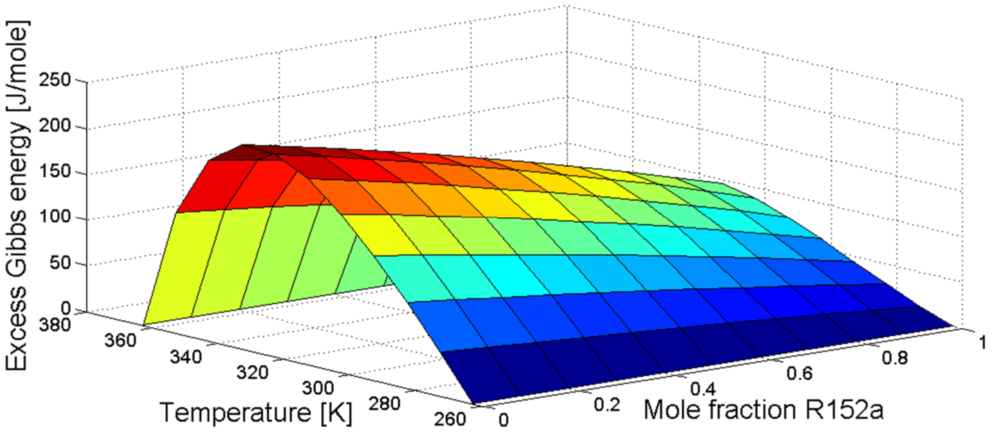

Fig.1. Excess Gibbs energy predicted for the system R152a (1) and R365mfc (2) by modified UNIFAC.

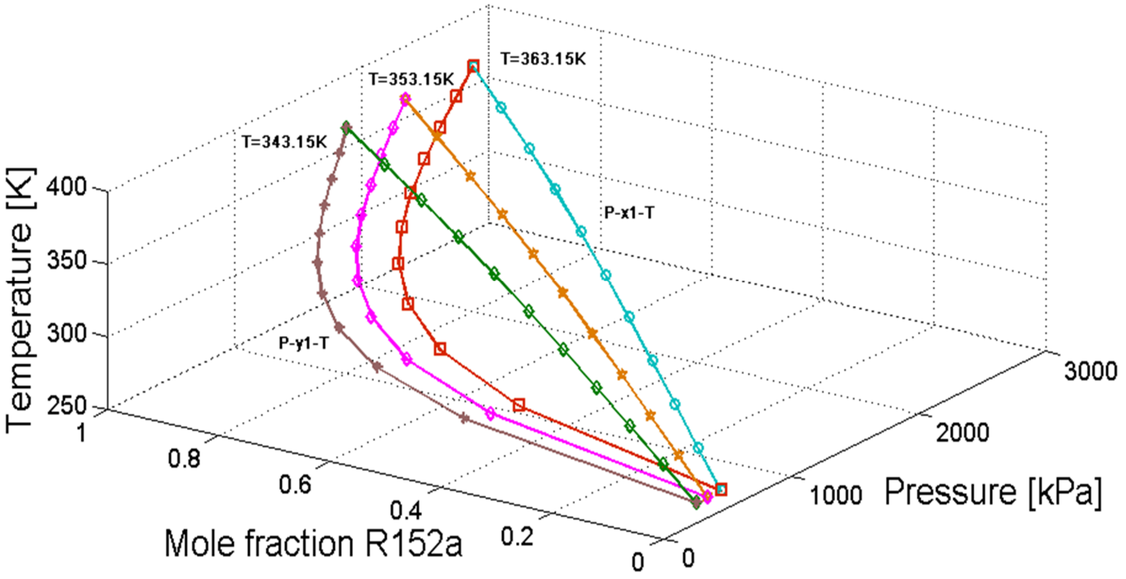

Fig.2. P-T-xy diagram from modified UNIFAC for the system R152a (1) and R365mfc(2).

As a fundamental function in the field of thermodynamics, Fig.1 illustrated the prediction of excess Gibbs energy for the system R152 and R365mfc as a function of temperature and composition relative to more volatile component R152a by modified UNIFAC method. It is to be mentioned that function is strongly dependent on composition and temperature of mixture. The function probably increases as temperature and composition increase in a rising curve until reaching certain composition of 0.7, and the curve then exhibits inverted character while reaching the ideal behavior of pure component upon which its value turns into a zero. Excess Gibbs energy function implies different effects involved in the mixing of various molecules and gives the energetic effect to molecules due to the variation of intermolecular forces and also the entropic effect presented by excess entropy function. This results from a lack of complete randomness in distribution of molecule in mixture. The equilibrium state of the system R152a and R365mfc is presented in a three dimensional P-T-composition diagram for temperature range 263.15K-363.15K in Fig.2. This figure shows schematically the P-T-composition surfaces which contain the equilibrium states of saturated vapor and saturated liquid for this binary mixture, where R152a is the more volatile component and R365mfc is the less volatile component. The lower surface contains the saturated vapor states which known as P-T-y surface. The upper surface contains the saturated liquid states which known as P-T-x surface.

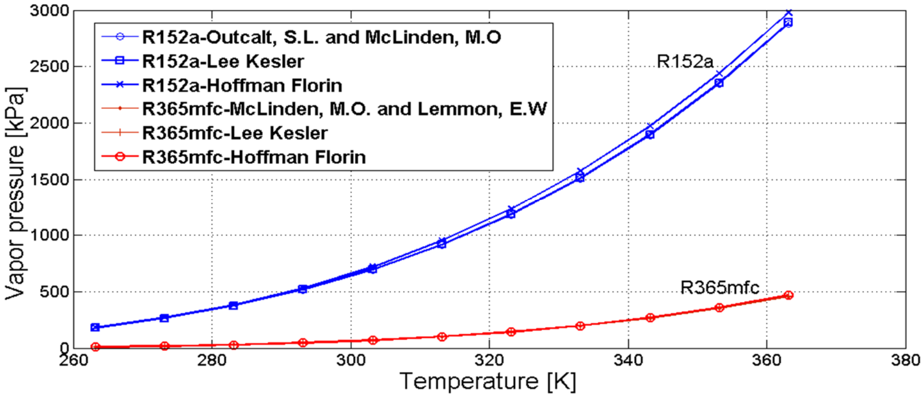

Fig.3. Saturation pressure temperature diagram of R152a and R365mfc.

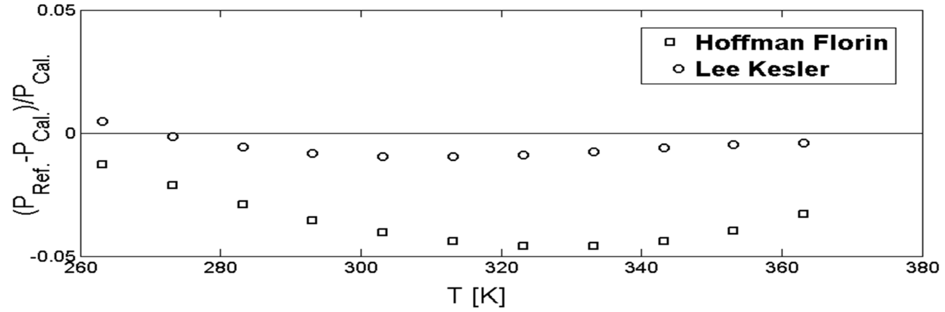

Fig.4. Relative deviation to experimental data in [17] [18] for saturation pressure of R152a.

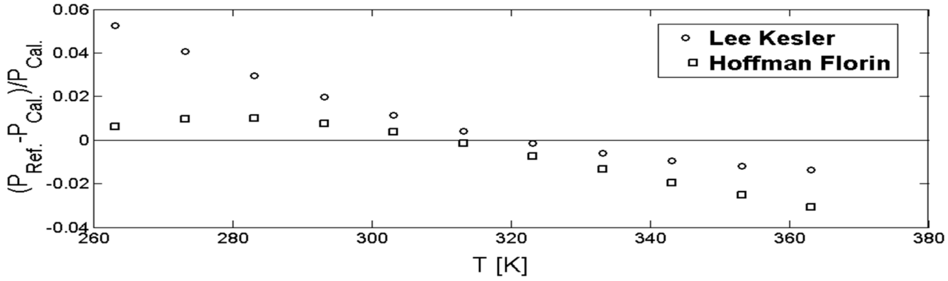

Fig.5. Relative deviation to experimental data in [17] [18] for saturation pressure of R365mfc.

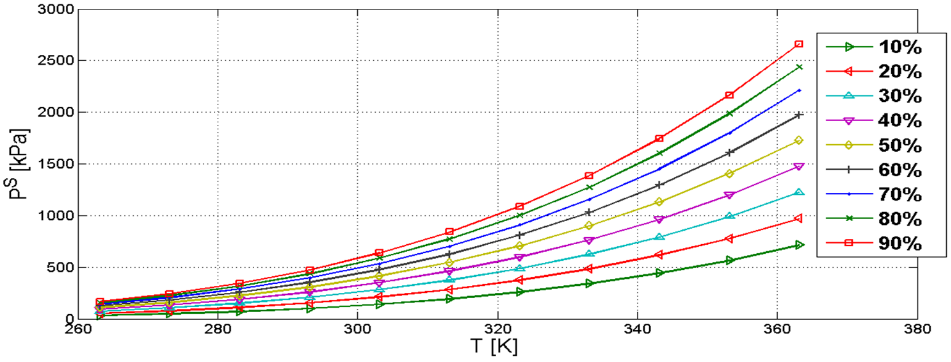

Fig.6. Bubble pressure temperature diagram of the system R152a (1) and R365mfc (2) from modified UNIFAC method.

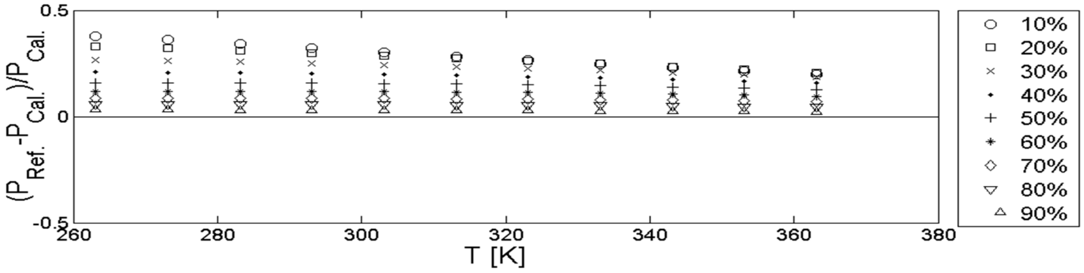

Fig.7. Relative deviation in saturation pressure measurement of the system R152a (1) and R365mfc (2), the data compared with data obtained from modified UNIFAC [19][20] method and the data of Mc Linden, M.O. and Lemmon et al. (NIST) [17] [18].

Obviously seen in Fig.3 and Fig.5 , the pure fluid data exhibited a minimum relative deviation in pressure for the temperature range of T=263.15K to T=363.15K. The model of Lee and Kesler (LK) have shown good results for fitting the light component R152a, maximum positive deviation less than 1% was provided by Lee Kesler. Whereas the model of Hoffman Florin (HF) yielded good results for R365mfc, maximum positive deviation of 2.85% was provided by Hoffman Florin. The relative deviation in the case of the mixture as shown in Fig.7 has indicated a high deviation on the way of increasing the mixture compositions. This mixture pressure data were compared with the pressure obtained from modified UNIFAC as presented in Fig.6 and the data of Mc Linden, M.O. and Lemmon et al (NIST) [17] [18].

IV. CONCLUSIONS

The work has delivered various thermodynamic data concentrating on the Excess Gibbs energy function and the saturation pressure of the environmentally friendly system of R152a and R365mfc. The liquid phase behavior of the mixture was investigated using the group contribution method of modified UNIFAC, which proved its reliability to predict the excess Gibbs free energy model. The work has also explored predictive models for the saturation pressure, namely the Lee Kesler and Hoffman-Florin, beside the high precision fundamental equations of state by Outcalt and McLinden from National Institute of Standard and Technology (NIST). The simulation results achieved good agreement with the experimental data by Outcalt and McLinden (NIST).

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.
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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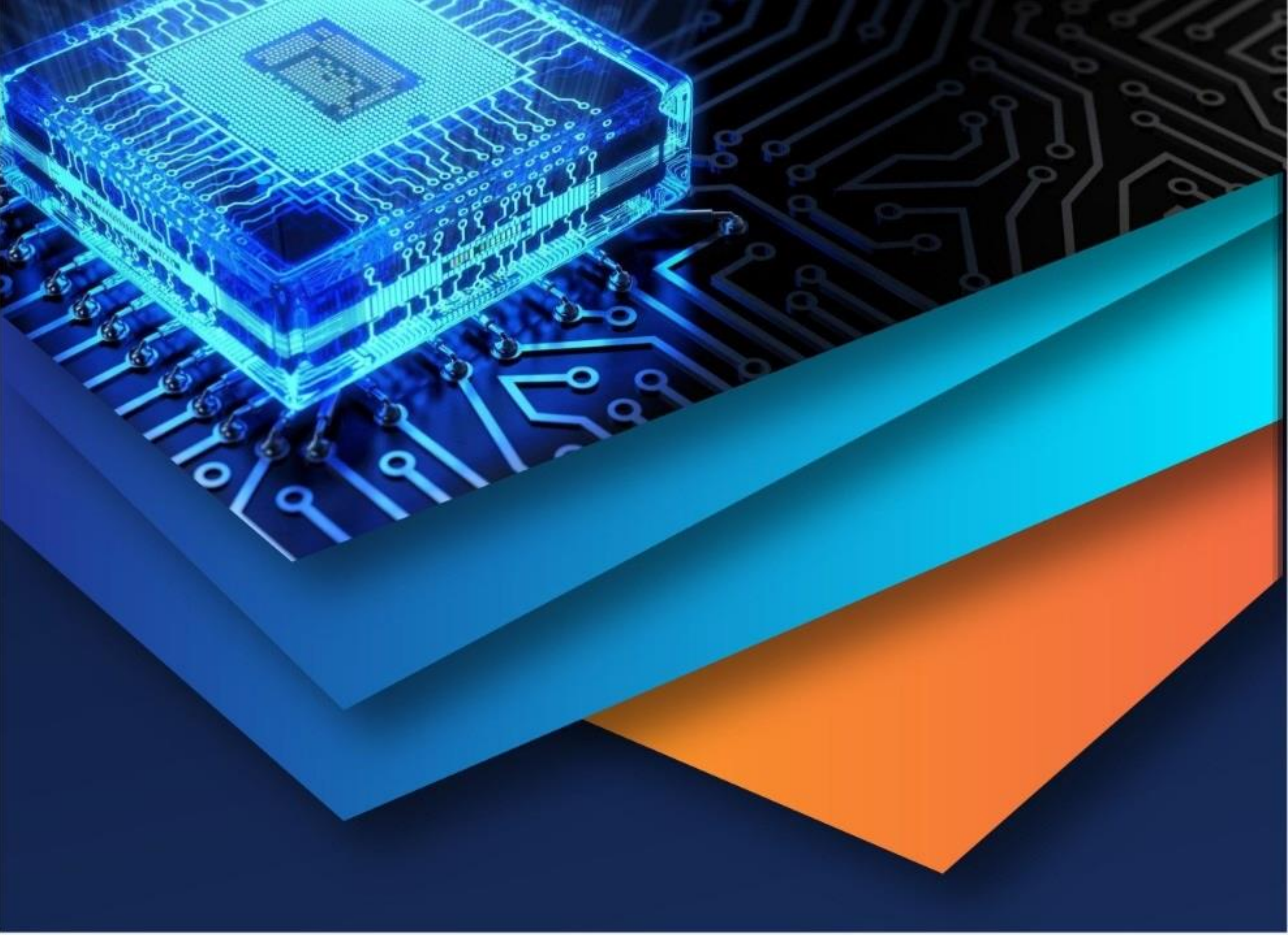

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