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Vapor–Liquid Equilibrium Data for the Binary System of Ethylene Glycol with Butanol At 94, 50, 10 KPA

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Abstract--Vapor–liquid equilibrium (VLE) data for Ethylene Glycol with Butanol are measured at pressure of 94, 50, 10 kPa by using a dynamic recirculation still. The experimental VLE data were tested to be thermodynamically consistent by point to point test. The experimental VLE data are well correlated by the Wilson, NRTL and UNIQUAC models and binary interaction parameters were determined by minimizing suitable objective function. No azeotrope was observed in system and appears easy to separate using conventional distillation method.
Keywords- VLE, Wilson, NRTL and UNIQUAC

I. INTRODUCTION

Ethylene glycol is used in antifreezer production as well as in polymer ester manufacturing.[1] Nowadays, Butanol is being used as petroleum additive. Using the coal instead of the crude oil as raw material for manufacturing of alcohol costs less and produced by using renewable resources. The butanol is used in pharmaceutical industry, photographic industry and in paint industry as varnish. It is also used in chlorination processes and in the organic synthesis of esters. Due to recent advances in the fermentation process for alcohol production, Butanol produced from biomass source has emerged as a promising fuel candidate in the transportation sector. Butanol used as petroleum additive has several advantages including higher energy density, lower vapor pressure, lower affinity to water and the ability to be transported via existing fuel distribution pipelines.[2] Hence vapor liquid equilibrium data for ethylene glycol with butanol at different pressure will be useful in modeling and simulation of separation processes of these to components.

II. EXPERIMENTAL SECTION

A. Materials

Detail specifications of various chemicals used for experimentation are listed in Table 1. The chemicals were used directly without any further purification. Table 2 contains the reported and experimental refractive index (n_D), boiling points (T_b) and Table 3 Antoine constants of the chemicals used.

TABLE I
COMPONENT, SUPPLIER AND PURITY

Chemical name	Source	Purity (mass %)
Ethylene Glycol	Loba chemicals	0.99
Butanol	Loba chemicals	0.99

TABLE II
REFRACTIVE INDICES (n_D) & BOILING POINT (T_b) OF PURE CHEMICALS

Chemical		n_D at (298.5K)	T_b/K (at 101.3 kPa)
Ethylene Glycol	Present work	1.42997	470.38
	Literature	1.4308[4]	470.27[4]
	Literature	1.4306[4]	470.45[4]
Butanol	Present work	1.39688	391.05
	Literature	1.3973[3]	390.83[3]
	Literature	1.3971[3]	390.75[3]

[a]Standard uncertainties u are u (n_D) = 0.002, u (T) = 0.1 K.

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TABLE III
ANTOINE CONSTANTS

Chemical	Antoine constants			units	reference equation
	A	B	C		
Ethylene Glycol	15.4119[1]	3928.97[1]	-106.38[1]	P=kPa, T=K	1
Butanol	6.4296[2]	1261.325[2]	106.43[2]	P=kPa, T=K	2

$$ln\ (P_i^{sat}/kPa) = A - \left(\frac{B}{C+(T/K)}\right) \quad (1)$$

$$log\ (P_i^{sat}/kPa) = A - \left(\frac{B}{(T/K)-C}\right) \quad (2)$$

III. APPARATUS AND PROCEDURE

The present work uses a dynamic recirculation type glass VLE apparatus proposed by Mali et. al [5]. The apparatus comprised of a boiling chamber, a Cottrell tube with vacuum jacket, an equilibrium chamber with vacuum jacket, a condenser, a condensate receiver and a equilibrium liquid-vapor condensate mixer. Vacuum jacket is provided to the Cottrell tube and the equilibrium chamber to avoid heat losses. Binary liquid mixture is initially fed to the boiling chamber which was provided with an external electrical heater. Suitable heating rate is set for the heater with the help of a rheostat attached to the heater. Vapor-liquid mixture rises up to the equilibrium chamber through the insulated Cottrell tube. Equilibrium chamber is packed with glass ball packing to enhance vapor-liquid contact area. Vapor-liquid comes in equilibrium with each other because of sufficient contact time and contact area provided jointly through the Cottrell tube and the equilibrium chamber. Temperature measurement is provided in the equilibrium chamber to sense the vapor-liquid equilibrium temperature.

In the equilibrium chamber, vapor and liquid separates and vapor heads towards the condenser and get condensed with a suitable cooling medium circulated through the condenser. The vapor condensate is collected in a receiver and overflows to the mixing chamber where is mixed with the liquid from the equilibrium chamber. Both, the vapor condensate receiver and the mixing chamber, are provided with magnetic stirrers to avoid any concentration gradient. The mixed liquid flows back to the boiling chamber to complete the circulation loop. Sufficient time is given for the vapor-liquid circulation so that equilibrium is achieved which is indicated by a constant temperature in the equilibrium chamber. Once a constant temperature is achieved, samples are collected for equilibrium liquid from the equilibrium chamber and equilibrium vapor from the condensate receiver. When the composition of the consecutive samples collected was constant, attainment of vapor-liquid equilibrium was confirmed and the experiment was stopped. While withdrawing samples, a very small quantity (>1mL) was withdrawn to ensure that equilibrium does not get disturbed. Similar experimental procedure was followed for all binary compositions.

IV. SAMPLE ANALYSIS

Samples were analyzed for the composition with the help of refractive index measurement. To estimate sample composition using refractive index, first a calibration curve of refractive index (n_D) versus mole fraction was generated. The calibration curve was generated by generating refractive index data at 293.15 K for known compositions of binary mixtures covering entire composition range. Refractive index was measured by a refractometer from Atago (model-RX-7000i) with an accuracy of ±0.0001 and resolution of 0.00001. Equations for the calibration curve were obtained by fitting a suitable polynomial equation using Microsoft Excel software. The composition of the equilibrium samples were estimated by measuring the refractive index and solving the calibration equation.

V. DATA REDUCTION

At experimental pressure of 93.13 kPa, the vapor phase could be assumed as an ideal gas. Therefore, modified Raoult's law (eq. 3) that takes into account liquid phase non ideality only can be applied to VLE calculations.[6]

$$y_iP = x_i\gamma_i P_i^{sat} \quad (i=1, 2, 3,\ldots n) \quad (3)$$

where, x_i and y_i are the liquid and vapor phase mole fraction of component i in equilibrium state, P is the total pressure, γ_i is the activity coefficient of component I in the liquid phase, and P_i^{sat} is pure component vapor pressure. The vapor pressure of the pure components used in the vapor–liquid equilibrium calculations are obtained through the Antoine equation (eq. 1 & 2). Antoine constants required for calculating vapor pressure are given in Table 3.

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The liquid-phase activity coefficients γ_i were estimated using activity coefficient models such as Wilson, NRTL and UNIQUAC. The experimental activity coefficient was calculated using eq. 4 which is obtained by rearranging eq. 3.

$$\gamma_i^{exp} = \frac{y_i P}{x_i P_i^{sat}} \quad (4)$$

VI. RESULTS AND DISCUSSION

The calibration curves were generated by measuring n_D at 293.15 K for various different compositions of binary mixture (Ethylene Glycol + Butanol) covering complete composition range and are as given in Figure 1. The samples were prepared with an electronic weighing balance with an uncertainty of ±0.1 mg. A suitable polynomial equation was fitted to the experimental n_D vs. mole fraction data using Microsoft Excel to obtain polynomial constants of the equation. The polynomial equations used for composition measurement are given in Table 4. The experimental n_D for various different binary mixtures (mole fractions) used for generating calibration curve is listed in Table 5.

TABLE IV
POLYNOMIAL EQUATION FOR CALIBRATION CURVE

Binary Pair	Calibration curve	Polynomial equation	R^2
Ethylene Glycol + Butanol	Figure 1	$y = 0.3776x^6 - 1.0735x^5 + 1.112x^4 - 0.502x^3 + 0.1037x^2 + 0.0143x + 1.399$	0.9998

TABLE V
MEASURED REFRACTIVE INDICES FOR VARIOUS ETHYLENE GLYCOL MOLE FRACTIONS[a]

Sr. no.	Ethylene Glycol (mole fraction) (x_1)	n_D
1	0.0000	1.3989
2	0.0436	1.3999
3	0.1186	1.4015
4	0.2361	1.4041
5	0.3124	1.4059
6	0.3274	1.4064
7	0.3574	1.4072
8	0.3915	1.4081
9	0.4872	1.4107
10	0.5509	1.4128
11	0.6602	1.4171
12	0.7393	1.4201
13	0.8361	1.4239
14	0.8819	1.4256
15	0.8955	1.4262
16	0.9620	1.4287
17	1.0000	1.4313

[a]Standard uncertainties u are u(T) = 0.1 K, u(x) = 0.001, u(n_D) = 0.002.

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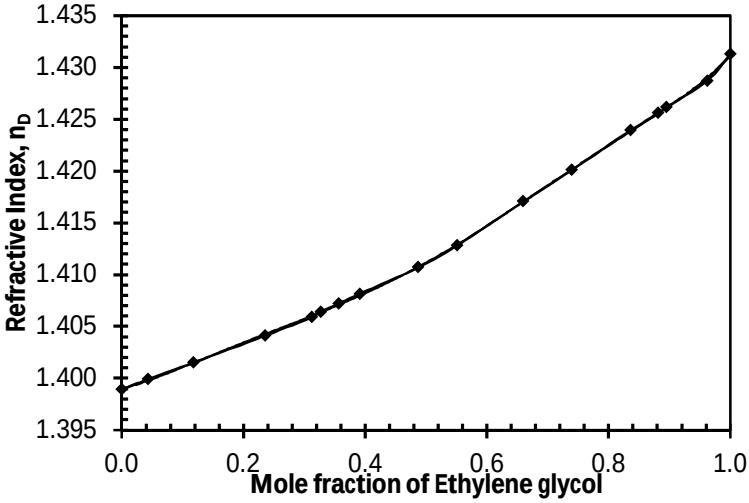

Fig 1. Calibration curve for Ethylene Glycol (1) + Butanol (2) system. ✖, measured n_D at 293.15 K vs. mole fraction of Ethylene Glycol; ---, third order polynomial

The experimental VLE data along with experimental activity coefficient for Ethylene Glycol + Butanol system at pressure 10, 50 and 94 kPa is listed in Table 6, 7 and 8. Uncertainty of n_D measurement (±0.0001) and the fitting accuracy of calibration curve contribute to the uncertainty of molar fraction measurement of the samples. In the present work, each sample was analyzed at least three times, and the average uncertainty in mole fraction was estimated which turned out to be ±0.001.

The experimental VLE data for the system was regressed with Wilson, NRTL and UNIQUAC activity coefficient models for minimizing the objective function given by eq.5 to estimate the binary interaction parameters.

$$OF = \sum_{i=1}^{N} \left(\frac{Y_i^{exp} - Y_i^{cal}}{Y_i^{exp}} \right)^2 \quad (5)$$

where, N is the number of data points, Y_i^{exp} is the experimental vapor mole fraction of component i and Y_i^{cal} is the calculated vapor mole fraction of component i using the activity coefficient model with estimated interaction parameters. While regressing NRTL model one of the three parameter of the model (α) was kept constant at 0.3. The r and q parameters which are structural volume and area parameter for the UNIQUAC model, respectively, used for regressing UNIQUAC model are listed in Table 11. The binary interaction parameters (BIP) obtained through regression for Wilson, NRTL and UNIQUAC are given in Table 12. The fitting of various different activity coefficient models to the experimental data is shown in Figure 2, 3 and 4. No azeotropic behavior was seen for the system. In fact, vapor and liquid composition curves are quite apart and no pinch was observed for all systems which indicate an easy separation using conventional distillation column with less number of equilibrium stages. The thermodynamic consistency of the experimental VLE data for the binary system was checked by the point to point consistency test. The criterion of consistency test is given in Table 09 and results of consistency test are given Table 10. Data was found thermodynamically consistent and suitable for process modeling.

TABLE VI

EXPERIMENTAL VLE DATA FOR ETHYLENE GLYCOL (1) + BUTANOL (2) AT 10 KPA[a]

T/K	x_1	y_1	γ_1	γ_2
338.74	0.0000	0.0000		1.000
340.66	0.0764	0.0208	10.583	0.957
343.19	0.1471	0.0405	8.956	0.889
346.22	0.2597	0.0496	5.041	0.869
349.61	0.4039	0.0543	2.820	0.907
352.05	0.4799	0.0607	2.262	0.917
356.20	0.6072	0.0778	1.757	0.980
358.87	0.6644	0.0878	1.534	1.003
369.04	0.8438	0.1448	1.091	1.294

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373.22	0.8841	0.1821	1.035	1.402
381.65	0.9322	0.2941	1.010	1.483
393.42	0.9681	0.5431	1.001	1.323
406.09	1.0000	1.0000	1.000	

[a]Standard uncertainties u are $u(x_1) = 0.001$, $u(y_1) = 0.001$, $u(T) = 0.1$ K, $u(P) = 0.1$ kPa.

TABLE VII

EXPERIMENTAL VLE DATA FOR ETHYLENE GLYCOL (1) + BUTANOL (2) AT 50 KPA[a]

T/K	x_1	y_1	γ_1	γ_2
373.06	0.0000	0.0000		1.000
373.45	0.0551	0.0052	2.338	1.036
375.25	0.1450	0.0150	2.326	1.054
378.02	0.2531	0.0303	2.323	1.064
381.50	0.3938	0.0515	2.110	1.120
384.20	0.4811	0.0650	1.898	1.164
388.15	0.5945	0.0911	1.765	1.251
391.42	0.6741	0.1085	1.580	1.356
398.13	0.8106	0.1556	1.372	1.749
408.79	0.8964	0.2553	1.267	1.984
420.55	0.9493	0.3934	1.133	2.306
432.15	0.9807	0.5864	1.048	2.966
448.03	1.0000	1.0000	1.000	

[a]Standard uncertainties u are $u(x_1) = 0.001$, $u(y_1) = 0.001$, $u(T) = 0.1$ K, $u(P) = 0.1$ kPa.

TABLE VIII

EXPERIMENTAL VLE DATA FOR THE ETHYLENE GLYCOL (1) + BUTANOL (2) AT 94 KPA[a]

T/K	x_1	y_1	γ_1	γ_2
389.46	0.0000	0.0000		1.000
389.71	0.0718	0.0049	1.366	1.063
391.22	0.1350	0.0099	1.365	1.075
394.88	0.2499	0.0217	1.360	1.076
398.48	0.3804	0.0376	1.308	1.132
401.17	0.4719	0.0519	1.288	1.194
404.27	0.5782	0.0668	1.177	1.329
407.57	0.6845	0.0859	1.107	1.563
411.23	0.7657	0.1120	1.102	1.821
421.65	0.8905	0.1994	1.102	2.563
441.09	0.9639	0.4280	1.060	3.255
450.21	0.9851	0.5963	1.058	4.406
467.88	1.0000	1.0000	1.000	

[a]Standard uncertainties u are $u(x_1) = 0.001$, $u(y_1) = 0.001$, $u(T) = 0.1$ K, $u(P) = 0.1$ kPa.

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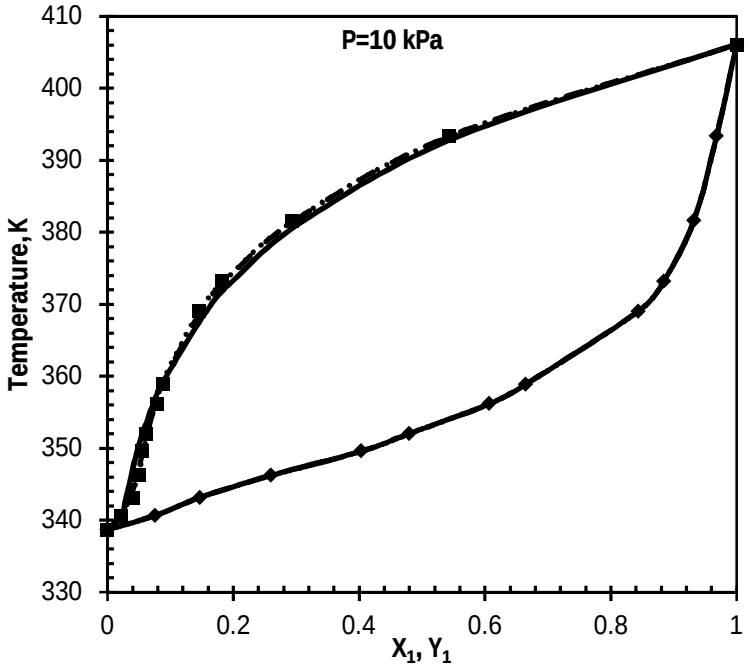

Fig 2. Txy plot for the Ethylene Glycol (1) + Butanol (2); ■, T−y (experimental at 10 kPa); ♦, T−x (experimental at 10 kPa); - - -, NRTL model; ——, Wilson model; ·····, UNIQUAC model

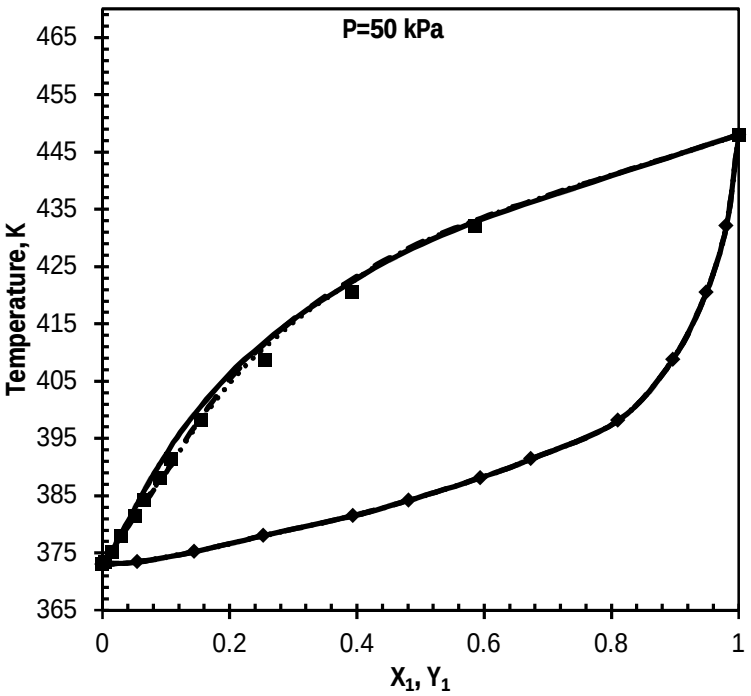

Fig 3. Txy plot for the Ethylene Glycol (1) + Butanol (2); ■, T−y (experimental at 50 kPa); ♦, T−x (experimental at 50 kPa); - - -, NRTL model; ——, Wilson model; ·····, UNIQUAC model

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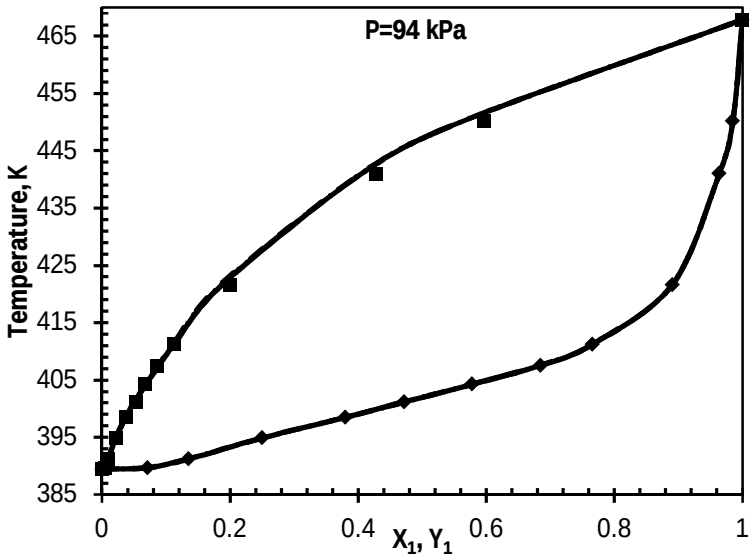

Fig 4. Txy plot for the Ethylene Glycol (1) + Butanol (2); ■, T−y (experimental at 94 kPa); ♦, T−x (experimental at 94 kPa); - - -, NRTL model; ——, Wilson model; ·····, UNIQUAC model

TABLE IX
CRITERIA OF THE CONSISTENCY TEST FOR POINT-TO-POINT METHOD[5]

Sr. no.	Parameter	Formula	Criteria
1	Overall deviation in vapor composition	$\Delta y=\frac{1}{N}\sum_{i=1}^{n}(y_{i,j}^{cal}-y_{i,j}^{exp})$	$\Delta y\leq 0.01$
2	Overall deviation in total system pressure	$\Delta P=\frac{1}{N}\sum_{i=1}^{n}(P_{i}^{cal}-P_{i}^{exp})$	$\Delta P\leq 1.33$

TABLE X
POINT-TO-POINT CONSISTENCY TEST RESULTS

Sr. no.	Pressure (kPa)	Binary system	Δy	ΔP
1	10	Ethylene Glycol +Butanol	0.0083	1.2234
2	50		0.0010	0.3629
3	94		0.0056	0.7856

TABLE XI
r AND q VALUES FOR UNIQUAC MODEL

Sr. no.	Chemical	r	q
1	Ethylene Glycol	2.4088[7]	2.2480[7]
2	Butanol	3.9243[8]	3.6680[8]

TABLE XII
BINARY INTERACTION PARAMETERS FOR DIFFERENT MODELS

Pressure (kPa)	Binary System	Interaction parameter	NRTL[a]	Wilson[b]	UNIQUAC[c]
10	Ethylene Glycol +Butanol	A_{12}	7747.11	9462.73	988.54
		A_{21}	4813.55	2756.48	2821.87
		α	0.3		

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50	Ethylene Glycol +Butanol	A_{12} A_{21} α	1690.31 -692.60 0.3	1610.21 7032.66	7112.06 -1455.96
94	Ethylene Glycol +Butanol	A_{12} A_{21} α	-189.14 5542.53 0.3	6878.23 -2634.16	2727.01 -1217.97

[a]The interaction parameters for the NRTL model: $A_{12}(J.mol^{-1}) = (g_{ij} - g_{ii})/R$.
[b]The interaction parameters for the Wilson model: $A_{12}(J.mol^{-1}) = (\lambda_{ij} - \lambda_{ii})/R$.
[c]The interaction parameters for the UNIQUAC model: $A_{12}(J.mol^{-1}) = (U_{ij} - U_{ii})/R$.

VII. CONCLUSIONS

The isobaric VLE data for binary system of Ethylene glycol with Butanol was measured using a dynamic recirculation still at pressures of 10, 50, 94 kPa. The VLE data was found thermodynamically consistent according to the point-to-point test. The experimental VLE data was correlated by the Wilson, NRTL and UNIQUAC activity coefficient models and all models fitted well. As no azeotrope was observed in any system, conventional distillation can be employed for separation of these mixtures. VLE plots also indicate that separation of the system with conventional distillation column would be easy with significantly less number of stages.

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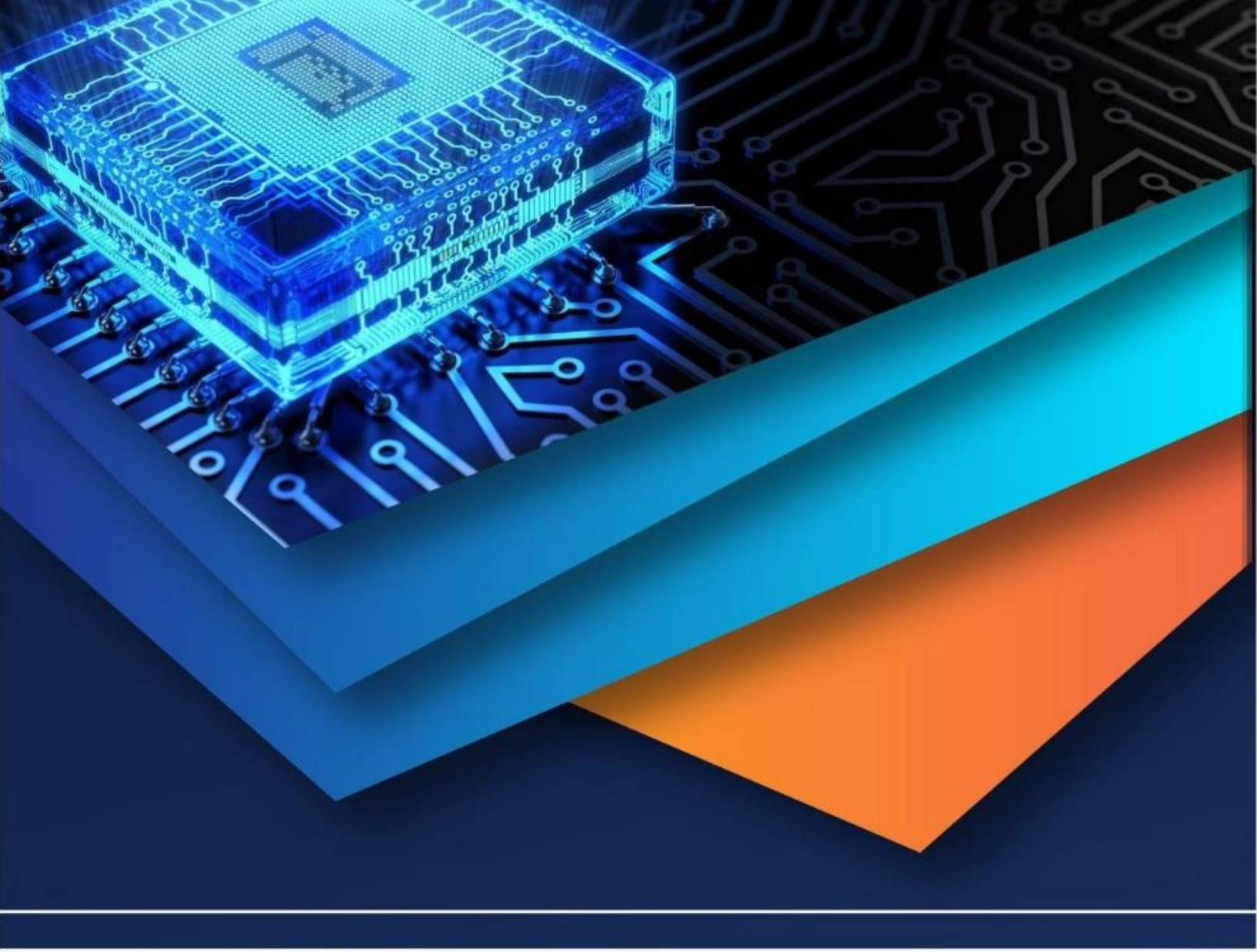

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