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Excess Thermodynamic Properties and Molecular Interaction in Ternary Systems of Aniline at 303.15K

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Abstract: Densities and viscosities of ternary liquid mixtures of Aniline with two polar solvents viz. Methyl ethyl ketone and N, N-Dimethylformamide and three non-polar solvents viz. benzene, toluene and carbon tetra chloride as well as their pure components have been determined at constant temperature 303.15 K. Excess thermodynamic properties viz. the excess viscosity (η^E), the excess molar volume (V^E), the excess Gibbs free energy of activation of flow ($\Delta G^{E\#}$) and an interaction parameter d by Grunberg and Nissan, have been calculated as a function of composition of ternary mixtures. Results have been revealed as evidence of the type and magnitude of molecular interactions existing among the components. The values of (η^E) and (V^E) are negative for all six systems over the entire range of composition. The values of ($\Delta G^{E\#}$) and d are negative for the systems with methyl ethyl ketone as a second component, while it is positive for the systems with N,N-Dimethylformamide as a second component except at lower concentration of second component where the value of ($\Delta G^{E\#}$) is negative.
Keywords: Density, viscosity, excess thermodynamic properties, molecular interactions, ternary liquid mixtures.

I. INTRODUCTION

The study of viscous behavior of liquid mixtures provide information regarding molecular interactions between the components of the mixtures by giving the data of thermodynamic and excess thermodynamic properties of the system [1], [2]. These include the excess molar volume (V^E), the excess viscosity (η^E), excess Gibbs free energy ($\Delta G^{E\#}$), excess enthalpy (ΔH^E), excess entropy (ΔS^E) etc. The literature concerning these excess properties has been exhaustive after the pioneering work of Prigogine [3]. During the last few decades studies of thermodynamic properties of liquid mixtures in the investigation of nature of molecular interaction between ions, dipoles, hydrogen bonding, multipolar and dispersive forces and physio-chemical behavior of the same, have been achieved merit able importance. Data developed in the studies has been widely used to comprehend the nature and extent of interactions [4] and understand the deviation of real liquid mixture from the ideality [5]-[7]. The deviation from ideal behavior may be either adhesive or cohesive forces between the mixing components [8]. Thermodynamic properties of liquid mixtures are useful in calculations involving chemical separations, heat transfer, mass transfer and fluid flow which are the requirement of the chemical industries [9],[10]. On the same time the information is useful in developing theories for liquid states and predictive methods for liquid mixtures as well as new industrial processes [11]. Study of mixtures of two or more liquid components is more useful than studying the pure component from industrial point of view as it provide the understanding of practical alteration in the medium for desired properties [12]. Aniline, a primary aromatic amine, is hugely used in industry [13], [14]. Hence it is worthwhile to study its flow behavior and excess thermodynamic properties with other components of industrial value. In literature, the comprehensive data of excess thermodynamic properties viz. η^E, V^E, $\Delta G^{E\#}$ and interaction parameter *d* on the ternary systems of Aniline is still lacking.

In present paper, Aniline has been selected as a first component with methyl ethyl ketone (MEK) / N, N-Dimethylformamide (N,N-DMF) (polar solvent) as a second component and benzene/ toluene / carbon tetra chloride (non-polar solvent) as third component separately in six different ternary systems. These are – i) Aniline + MEK + Benzene, ii) Aniline + MEK + Toluene, iii) Aniline + MEK + Carbon tetra chloride, iv) Aniline + N,N-DMF + Benzene, v) Aniline + N,N-DMF + Toluene, and vi) Aniline + N,N-DMF + Carbon tetra chloride. All systems have been studied at a constant temperature 303.15 K and values of ρ, η, η^E, V^E, $\Delta G^{E\#}$ and *d* have been calculated to predict the type and magnitude of molecular interactions in the systems under study.

II. MATERIALS AND METHODS

All chemicals used in the present study were of analytical reagent grade. No purification was carried out and chemicals were used directly as provided by manufacturer. Densities and viscosities of pure components as well as ternary mixtures were measured at experimental temperature **303.15 K**, using specific density bottle and Ostwald viscometer respectively. Purities of pure components

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were checked by comparing the experimental densities and viscosities of pure components with those reported in the literature [15]-[17]. All ternary mixtures were prepared volumetrically in stoppered flasks. 10 ml hypodermic syringe with 0.5 mm thick needle was used for measuring the liquids. During the mixture preparation, concentration of first component (Aniline) in all ternary mixture was kept in continuous increasing manner while that of second component was kept in decreasing then increasing and again decrease and increase way to observe the change in particular data with the change in concentration of the components. Consequently, the concentration of third component need to be changed. The heavier components were charged first to minimize the error due to evaporation. After preparing the ternary liquids mixtures, the flasks were left undisturbed for 2 hrs. to allow them to attain the equilibrium. After that the liquid mixtures were placed in electrically operated thermostat bath, set at temperature 303.15 K, for 1 hour, before using the mixtures for any measurement viz. density or viscosity. All the glassware used during whole experimental work were cleaned first with water, then hot water, then dried and again washed with acetone before every use.

III. THEORETICAL

The values of density (ρ), viscosity (η), molar volumes (V) and excess thermodynamic functions viz. the excess viscosity (η^E), the excess molar volume (V^E), The Gibbs free energy of activation of flow ($\Delta G^{\#E}$) and the interaction parameter (d) have been calculated as a function of composition of the ternary liquid mixtures.

The density (ρ) of the pure liquid as well as ternary mixtures were measured by filling density bottle with the liquid / ternary mixtures maintained at experimental temperature and calculated by using following expression:

$$\rho = \frac{w3-w1}{w2-w1}\,\rho w \qquad \ldots\ldots\ldots\ldots\ldots (1)$$

where $w1, w2$ *and* $w3$ are the weight of empty density bottle, weight of density bottle with water and weight of density bottle with pure liquid / ternary liquid mixture respectively. ρw is the density of water at experimental temperature 303.15 K.

The viscosities of organic liquid mixtures were measured using the Ostwald viscometer suspended in thermostat water bath maintained at 303.15 K. By comparing the flow time of pure liquids or ternary mixtures with that of water, the viscosity was calculated using following relation:

$$\eta = \frac{t}{tw} \times \frac{\rho}{\rho w} \times \eta w \qquad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

where ηw is the coefficient of viscosity of water, ρ and ρw are the densities, and t and tw are times of flow of mixture and water, respectively.

The mole fraction of a liquid is the ratio of molarity of the component liquid to that of the ternary liquid mixture. It is denoted by x and has no unit. If x_1, x_2 and x_3 are the mole fractions of component 1, 2 and 3 respectively, then they are defined as below –

$$x_1 = \frac{M1}{M1+M2+M3},\ x_2 = \frac{M1}{M1+M2+M3},\ x_3 = 1-(x_1 + x_2)$$

where *M1*, *M2* and *M3* are molarities of component 1, 2 and 3 respectively. Molarity of any component is defined as

$$Molarity = \frac{volume\ of\ component \times density\ of\ the\ component}{molecular\ weight\ of\ the\ component}$$

Molar volume of a component liquid is the volume in milliliters occupied by one mole of the liquid and can be calculated by using the relation Molar volume (V) = Molecular weight (MW) / Density (ρ). Thus molar volume of ternary liquid was calculated using the following relation -

$$V = \frac{x_1 MW_1 1 + x_2 MW_2 + x_3 MW_3}{\rho} \qquad \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

where V and ρ are the Molar volume and Density of ternary mixture and MW_1, MW_2 and MW_3 are molecular weights of component 1, 2 and 3, respectively.

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The excess viscosity (η^E) of the selected ternary mixtures was determined by using the re relation –

$$\eta^E = \eta - (x_1 \eta_1 + x_2 \eta_2 + x_3 \eta_3) \qquad \text{…. …. …. …. ….(4)}$$

where η, η_1, η_2 *and* η_3 are the viscosities of ternary mixture, pure component 1, component 2 and component 3, respectively. While x_1, x_2 and x_3 are mole fractions of component 1, 2 and 3 respectively.

The excess molar volume (V^E) was determined with the following equation –

$$V^E = V - (x_1V_1 + x_2V_2 + x_3V_3) \qquad \text{…. …. …. …. ….(5)}$$

where V, V_1, V_2, V_3 are molar volumes of ternary mixture, component 1, 2 and 3 respectively and were obtained with relations $V_1 = MW_1 / \rho_1$, $V_2 = MW_2 / \rho_2$ and $V_3 = MW_3 / \rho_3$ where all characters have their usual denotations.

The Gibbs free energy of activation of flow ($\Delta G^{\#E}$) of ternary systems was computed from the Erying equation [18]. The resulting equation is given below –

$$\Delta G^{\#E} = [RT\ \{\ln\eta V - (x_1\ln\eta_1V_1 + x_2\ln\eta_2V_2 + x_3\ln\eta_3V_3)\}] \qquad \text{…. …. …. …. ….(6)}$$

Where the letters have their usual significance.

An interaction parameter (d) was also determined to outline the magnitude of molecular interaction between the molecules of the ternary mixtures nominated for the present study. It was calculated with the help of equation given by Grunberg and Nissan for binary liquid mixtures [19] which is as below –

$$\ln\eta = x_1\ln\eta_1 + x_2\ln\eta_2 + x_1x_2d$$

On applying this equation on ternary system, the equation takes the following form –

$$\ln\eta = x_1\ln\eta_1 + x_2\ln\eta_2 + x_3\ln\eta_3 + x_1x_2x_3d$$

$$\text{thus, } d = \frac{\ln\eta - (x_1 \ln\eta_1 + x_2 \ln\eta_2 + x_3 \ln\eta_3)}{x_1 x_2 x_3} \qquad \text{…. …. …. …. ….(7)}$$

where d is a constant, regarded as measure of strength of molecular interactions among the mixing components.

IV. RESULTS AND DISCUSSION

The values of ρ, η, η^E, V, V^E, $\Delta G^{\#E}$, and d for all six ternary systems have been presented in Table-1. The variation of ρ, η, η^E, V^E and $\Delta G^{\#E}$ along with the varying mole fraction of first component (x_1) i.e. Aniline have been plotted and displayed in Fig. (1-30). The results have been interpreted to trace the trend of molecular interaction depending on the increase or decrease of mole fractions of component one and two.

It is seen that densities and viscosities in each case are moving in non-linear manner. Values of both ρ and η are increasing with the increase in component-1 however differing at some places due to irregular change in concentrations of component-2 & 3, thus giving the curve. The non-linear variation of these physical properties with the change of the composition of mixtures indicates the presence of molecular interactions [20]-[22].

Table-1 : Experimental data of ρ, η, η^E, V, V^E, $\Delta G^{\#E}$, and d with the x_1 and x_2 of 6 Systems of Aniline at 303.15 K

System – 1: Aniline + MEK + Benzene

X_1	X_2	ρ	η	η^E	V	V^E	$\Delta G^{\#E}$	d
0.0492	0.7495	0.8345	0.4447	-0.1031	89.0976	-1.9374	-81.9550	-1.4962
0.0993	0.6493	0.8494	0.4944	-0.2024	89.1369	-1.9178	-135.8879	-2.0030
0.1485	0.5500	0.8632	0.5438	-0.2995	89.2582	-1.8063	-208.7325	-2.5466
0.1984	0.4495	0.8781	0.6066	-0.3852	89.2757	-1.7898	-252.5076	-2.5706
0.2475	0.1993	0.8951	0.7024	-0.4638	90.0812	-0.9023	-328.1666	-4.4239
0.2972	0.2497	0.9025	0.7434	-0.5427	89.8426	-1.2514	-360.4813	-3.8470
0.3307	0.3334	0.9017	0.7712	-0.5862	89.9074	-1.2670	-327.3437	-3.1560

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0.3470	0.1503	0.9133	0.8318	-0.6023	90.2443	-0.8512	-384.2319	-5.4816
0.4462	0.1003	0.9301	0.9922	-0.7092	90.5465	-0.6691	-418.7612	-7.8389
0.4964	0.1505	0.9315	1.0362	-0.7863	90.8888	-0.4198	-469.1178	-6.9156
0.5466	0.1508	0.9447	1.1612	-0.7918	90.4151	-0.9652	-415.8731	-6.2255
0.5974	0.2507	0.9464	1.2016	-0.8648	90.4256	-1.0877	-451.8731	-7.4018
0.6474	0.2006	0.9561	1.3450	-0.8607	90.6005	-0.9445	-432.2732	-8.2425
0.6982	0.2513	0.9624	1.4453	-0.8831	90.4991	-1.1673	-427.8776	-17.8028

System -2: Aniline + MEK + Toluene

X_1	X_2	ρ	η	η^E	V	V^E	$\Delta G^{\#E}$	d
0.0508	0.7750	0.8308	0.4310	-0.1092	92.2810	-1.8439	-99.3038	-3.1925
0.1035	0.6771	0.8442	0.4785	-0.2152	93.2008	-1.7369	-152.9352	-2.9249
0.1561	0.5786	0.8576	0.5282	-0.3188	94.0974	-1.6558	-221.3256	-3.0844
0.2104	0.4769	0.8735	0.6035	-0.4018	94.7782	-1.8266	-220.8573	-2.3079
0.2651	0.3743	0.8914	0.6885	-0.4763	95.2493	-2.2250	-233.5252	-2.0493
0.3209	0.2697	0.8994	0.7478	-0.5797	96.7930	-1.5579	-348.1916	-3.5603
0.3499	0.3526	0.9033	0.7821	-0.6098	94.5686	-1.9005	-308.4637	-2.8904
0.3780	0.1637	0.9144	0.8625	-0.6314	97.5889	-1.6414	-338.5289	-4.2916
0.4818	0.1083	0.9294	0.9837	-0.7924	97.3262	-1.1739	-514.2277	-9.1477
0.5266	0.1598	0.9379	1.0757	-0.8110	95.3762	-1.5025	-458.0208	-6.4594
0.5750	0.1587	0.9450	1.1603	-0.8554	94.7413	-1.3806	-486.4345	-7.5000
0.6126	0.2570	0.9482	1.2791	-0.8204	92.3843	-1.4542	-335.0226	-5.8434
0.6638	0.2057	0.9597	1.3949	-0.8473	92.3932	-1.4798	-392.2397	-8.0196
0.7040	0.2534	0.9627	1.5495	-0.7918	91.1692	-1.2581	-268.4470	-

System -3: Aniline + MEK + Carbon tetra chloride

X_1	X_2	ρ	η	η^E	V	V^E	$\Delta G^{\#E}$	d
0.0547	0.8339	0.9679	0.4890	-0.0891	85.0863	-6.8602	-35.8765	12.3160
0.1137	0.7434	1.0190	0.5545	-0.2030	84.5766	-7.6609	-125.7582	3.0307
0.1749	0.6481	1.0723	0.6304	-0.3138	84.1640	-8.3574	-221.3906	0.3043
0.2125	0.3573	1.3047	0.7974	-0.3713	85.6298	-8.7177	-358.4846	-1.4298
0.2412	0.5464	1.1189	0.7138	-0.4319	84.4959	-8.3412	-337.2164	-1.4360
0.3105	0.4384	1.1785	0.8205	-0.5366	84.1358	-9.0246	-457.6317	-2.3628
0.3430	0.2762	1.2936	0.9268	-0.5823	85.3703	-8.7410	-581.7674	-3.7310
0.3981	0.4013	1.1489	0.9694	-0.6080	84.3146	-8.5576	-391.5713	-1.8666
0.4641	0.2009	1.2731	1.0933	-0.7316	85.8106	-8.0825	-704.4071	-6.0971
0.5780	0.1300	1.2595	1.2867	-0.8353	85.8427	-7.8280	-810.5956	-10.7523
0.6268	0.2296	1.1537	1.4211	-0.7667	84.0937	-8.5593	-541.4498	-5.7731
0.6466	0.1778	1.1600	1.3844	-0.8686	86.3649	-6.5462	-712.3333	-10.3619
0.7014	0.2173	1.0677	1.5033	-0.8630	87.5681	-4.7019	-560.3963	-13.8368
0.7166	0.2580	1.0021	1.6022	-0.7800	89.0613	-2.8228	-313.4665	-20.1108

System – 4: Aniline + N,N-DMF + Benzene

X_1	X_2	ρ	η	η^E	V	V^E	$\Delta G^{\#E}$	d
0.0437	0.7774	0.9321	0.7677	-0.0644	80.3179	-0.5977	-16.9316	-0.2744
0.0896	0.6836	0.9332	0.8241	-0.1083	81.4734	-0. 6796	33.2716	1.3652
0.1361	0.5876	0.9358	0.8887	-0.1450	82.5073	-0.9034	90.0783	1.9818
0.1846	0.4877	0.9356	0.9389	-0.2006	83.8385	-0.8813	95.5550	1.5540
0.2394	0.2254	0.9230	0.9046	-0.3238	87.2985	-0.7549	-28.5576	-0.1633
0.2852	0.2800	0.9353	1.0180	-0.3406	86.5935	-0.8475	24.6441	0.4946
0.3133	0.3684	0.9485	1.1436	-0.3061	85.3665	-1.0174	121.8469	1.5633
0.3387	0.1706	0.9352	1.0324	-0.4431	88.0559	-0.8270	-89.1695	-0.9639

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0.4390	0.1149	0.9451	1.1610	-0.5638	89.0151	-0.6942	-183.3841	-2.9434
0.4844	0.1710	0.9574	1.3241	-0.5302	88.2901	-0.7876	-95.5867	-1.0779
0.5292	0.2266	0.9689	1.5147	-0.4674	87.6417	-0.8020	5.7590	0.3040
0.5733	0.2810	0.9794	1.7172	-0.3907	87.1001	-0.7312	89.7637	1.7520
0.6262	0. 2268	0.9822	1.8095	-0.4248	87.9372	-0.6422	35.4934	0.9019
0.6699	0.2817	0.9940	2.0604	-0.2988	87.2843	-0.6838	128.0246	6.1340

System – 5: Aniline + N,N-DMF + Toluene

X_1	X_2	ρ	η	η^E	V	V^E	$\Delta G^{\#E}$	d
0.0450	0.8007	0.9318	0.7966	-0.0376	82.5705	-0.7867	129.5155	6.7020
0.0930	0.7099	0.9327	0.8600	-0.0787	84.3954	-0.9210	203.6910	4.7768
0.1425	0.6154	0.9330	0.9122	-0.1342	86.3493	-0.9951	230.9076	3.2086
0.1950	0.5152	0.9322	0.9654	-0.1951	88.5257	-0.9784	246.6687	2.3569
0.2495	0.4110	0.9320	1.0120	-0.2669	90.7214	-1.0193	231.2412	1.6504
0.2695	0.2469	0.9177	0.9071	-0.3656	95.5636	-0.9112	96.7127	-0.3740
0.3070	0.3013	0.9309	1.0187	-0.3853	93.1434	-0.9722	105.4202	0.0704
0.3681	0.1855	0.9307	1.0265	-0.5105	95.5974	-1.0072	-31.0079	-1.8216
0.4734	0.1239	0.9409	1.1558	-0.6442	95.9184	-0.8301	-161.5387	-4.3691
0.5132	0.1811	0.9529	1.3487	-0.5703	93.6089	-0.7757	-32.6767	-1.5021
0.5512	0.2359	0.9670	1.5550	-0.4777	91.2039	-0.9181	70.6535	0.3613
0.5872	0.2878	0.9794	1.7890	-0.3514	89.0766	-0.9024	184.6618	3.0890
0.6416	0.2323	0.9861	1.8569	-0.4136	89.5976	-1.1672	76.7286	1.3671
0.6752	0.2839	0.9962	2.1537	-0.2180	87.7271	-0.9317	229.1107	11.9453

System – 6: Aniline + N,N-DMF + Carbon tetra chloride

X_1	X_2	ρ	η	η^E	V	V^E	$\Delta G^{\#E}$	d
0.0443	0.7882	1.0768	0.8864	0.0025	81.2667	-0.8189	158.0315	11.7341
0.0912	0.6962	1.1315	0.9956	0.0043	81.3856	-2.2575	229.7136	8.4172
0.1391	0.6007	1.1480	1.0772	-0.0414	84.3985	-0.8663	288.9898	5.4980
0.1896	0.5009	1.1857	1.1736	-0.0701	85.9373	-1.0292	306.7813	4.3717
0.2413	0.3975	1.2216	1.2753	-0.0964	87.6506	-1.0531	318.7736	3.8382
0.2953	0.2899	1.2559	1.3130	-0.1926	89.5875	-0.9628	184.9230	2.2516
0.3215	0.3781	1.1837	1.3841	-0.1748	87.6809	-0.9175	255.7376	2.9345
0.3521	0.1774	1.2884	1.3359	-0.3102	91.6765	-0.7622	15.7803	0.3713
0.4549	0.1191	1.2597	1.4840	-0.4049	92.5604	-0.4140	-69.0672	-1.0984
0.4982	0.1758	1.2035	1.6157	-0.3687	90.8963	-0.6627	10.2608	0.2940
0.5397	0.2310	1.1416	1.7417	-0.3341	89.7021	-0.4733	82.4865	1.2042
0.5799	0.2842	1.0856	1.8670	-0.2976	88.1404	-0.7194	129.8224	2.5158
0.6335	02294	1.0882	1.9656	-0.3275	89.0054	-0.6202	69.3406	1.5855
0.6723	0.2827	1.0311	2.2260	-0.1526	87.4929	-0.8240	260.6365	12.8701

A. *Excess viscosity (η^E)*

The excess viscosity (η^E) have been calculated with eq. (4) and values are presented in Table-1. The values of η^E are negative for all ternary mixtures over the entire range of composition. Negative values of η^E are the consequences of lower viscosity contribution of nonspecific interactions in non-ideal mixtures [20], [23]-[25]. The plots of (η^E) versus (x_1) have been presented in Fig. 3, 8, 13, 18, 23 and 28. The minima appearing in the figures indicate the maximum dispersion of unlike molecules [21], [26]. However, negative values in systems- 4, 5 and 6 start increasing to less negative after the minima in the plot which indicates the complex formation between the components at certain concentrations [27]-[30]. It has been also noticed that values of η^E in systems – 1, 2 & 3 are more negative than those in systems – 4, 5 & 6, again indicating that systems containing N,N-DMF as a second component are

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showing higher degree of molecular interactions. This may be attributed – i) to the presence of another amide group in second component, and ii) the presence of two $-CH_3$ functional groups, which effectively increasing the electron density and possibility of hydrogen bonding between unlike molecules due to compact geometrical rearrangement.

B. Excess molar volume (V^E)

The excess molar volume (V^E) have been calculated with eq. (5) and values are presented in Table-1. The plots of (V^E) versus (x_1) have been presented in Fig. 4, 9, 14, 19, 24 and 29. The values of V^E are negative for all ternary mixtures over the entire range of composition. Negative values arise due to increased interactions between the unlike molecules or due to very large difference in size of pure components [31], [32] which is applicable on the ternary systems under study. Recently more interpretations have been attempted to predict the molecular interaction based on values of V^E. Treszczanowicz *et.al.* [33] suggested three types of attributes of V^E values i) physical, ii) chemical, and iii) structural. Physical association contributes to the positive values due to non-specific interaction between the mixing components. Chemical association results in decrease of volume due to specific interactions and complex formation thus contributing to the negative values of V^E. The structural association suggest interstitial rearrangement between the mixing components and thus mostly contribute to the negative values of V^E. Kumari *et.al.* [34] suggested that negative and positive values of V^E are due to : (i) loss of dipolar association, (ii) difference in size and shape of the components, (iii) dipole–dipole, dipole-induced dipole interactions, and (iv) electron donor–acceptor complex formation. Positive values are arising mainly due to first two factors while negative values due to latter two factors. Negative of V^E values for all six systems under study may be attributed to the complex formation due to dipole and dipole-induced dipole interactions and interstitial rearrangement. It has also been noticed that values of V^E for the systems containing MEK as a second component are less negative for system-1, more negative for system-2 and highly negative for system-3, while in systems containing N,N-DMF as a second component values of V^E are negative but do not change much in magnitude.

C. Gibbs free energy of activation of flow ($\Delta G^{\#E}$)

The Gibbs free energy of activation of flow ($\Delta G^{\#E}$) has been calculated with eq. (6) and values are presented in Table-1. The plots of ($\Delta G^{\#E}$) versus (x_1) have been presented in Fig. 5, 10, 15, 20, 25 and 30. A perusal of Table-1 shows that the values of ($\Delta G^{\#E}$) in systems containing MEK as the second component are negative over the entire range of composition while positive in systems comprising N,N-DMF as a second component except at the lower concentration of second component where the values are negative. According to Oswal and Rao [35] the values of ($\Delta G^{\#E}$) may composed of three types of contributions:- i) dispersion forces or breaking of bonds of associated components contribute to the negative values, ii) specific interaction contribute to the positive values, and iii) difference in size of mixing components also contribute to the positive values. With this interpretation type of interaction can be identified as in systems containing MEK there is dominance of dispersion forces while systems with N,N-DMF are showing the presence of specific interaction.

Plots for system - 1

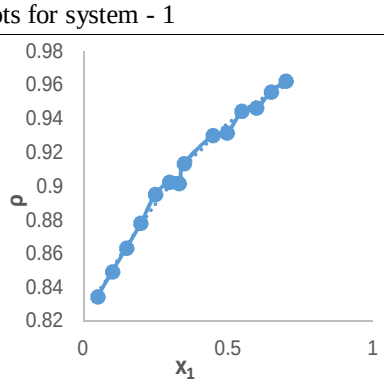

Fig.1. x_1 vs ρ

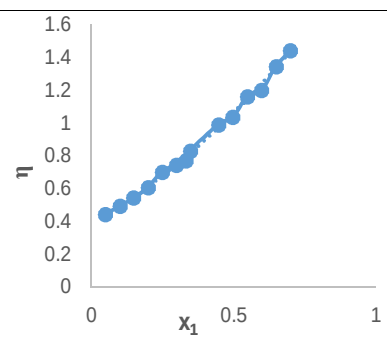

Fig.2. x_1 vs η

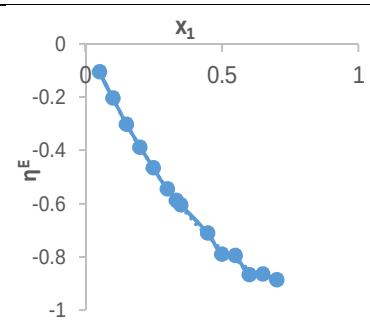

Fig.3. x_1 vs η^E

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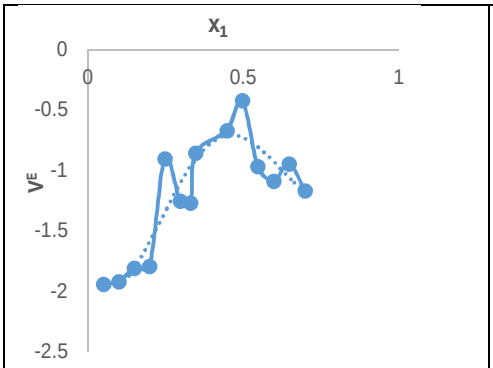

Fig.4. x_1 vs V^E

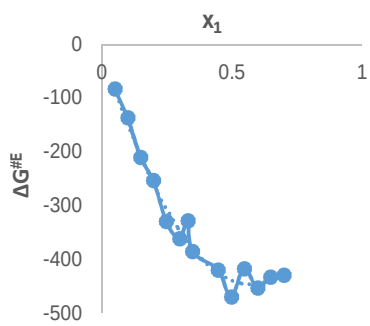

Fig.5. x_1 vs $\Delta G^{\#E}$

Plots for system - 2

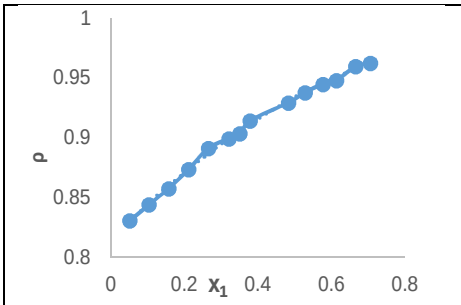

Fig.6. x_1 vs ρ

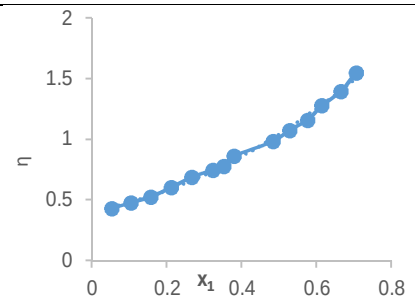

Fig.7. x_1 vs η

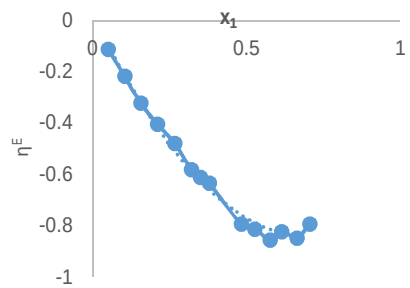

Fig.8. x_1 vs η^E

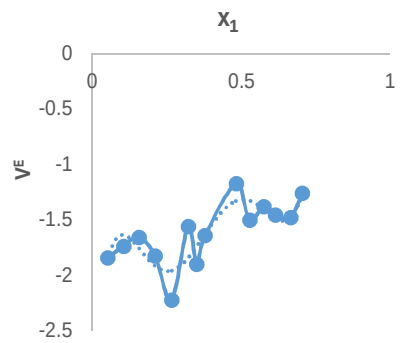

Fig.9. x_1 vs V^E

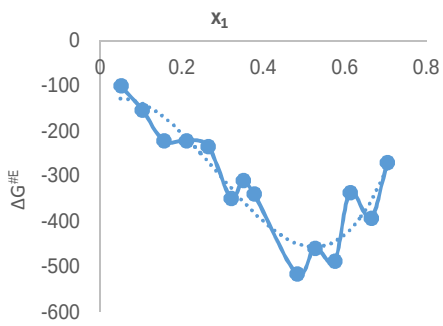

Fig.10. x_1 vs $\Delta G^{\#E}$

Plots for system - 3

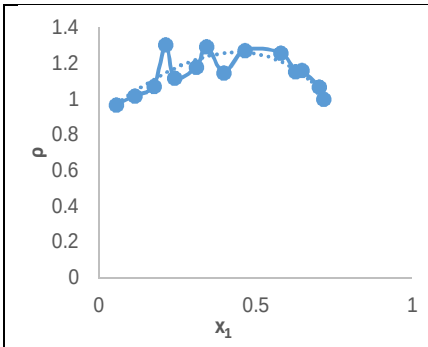

Fig.11. x_1 vs ρ

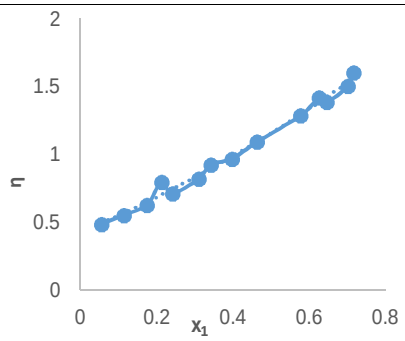

Fig.12. x_1 vs η

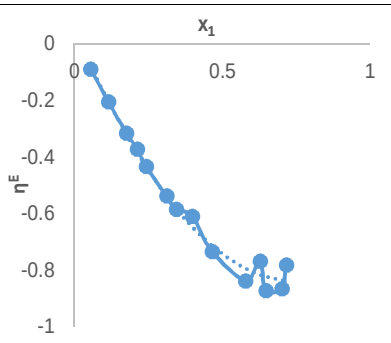

Fig.13. x_1 vs η^E

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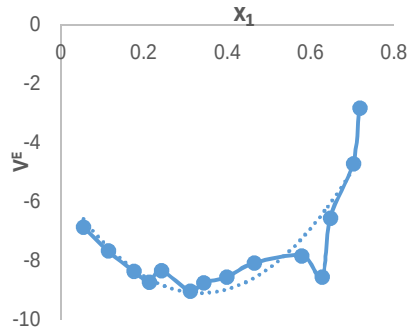

Fig.14. x_1 vs V^E

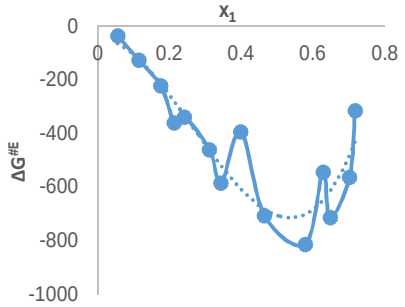

Fig.15. x_1 vs $\Delta G^{\#E}$

Plots for system – 4

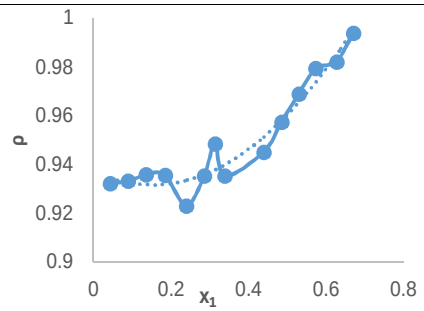

Fig.16. x_1 vs ρ

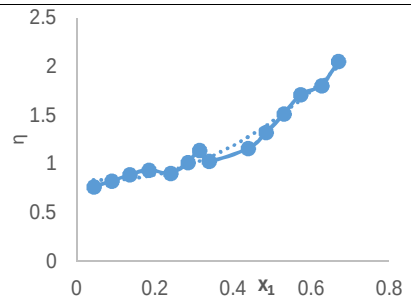

Fig.17. x_1 vs η

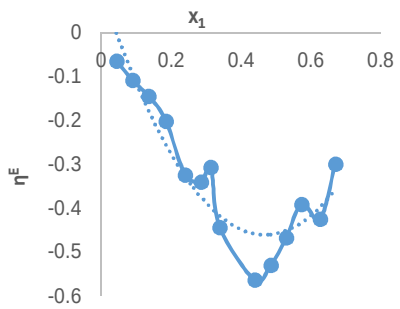

Fig.18. x_1 vs η^E

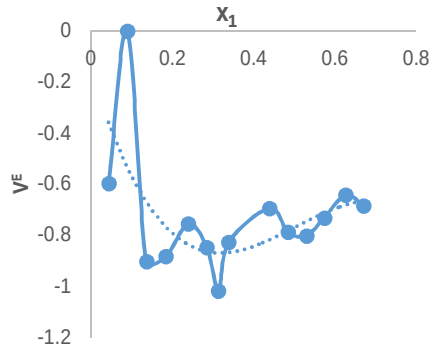

Fig.19. x_1 vs V^E

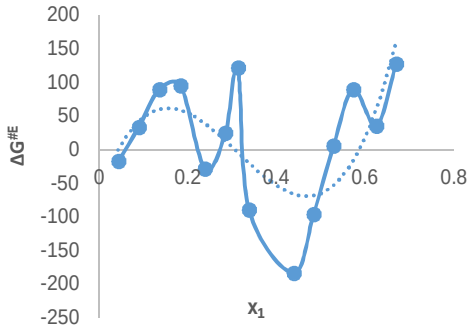

Fig.20. x_1 vs $\Delta G^{\#E}$

Plots for system - 5

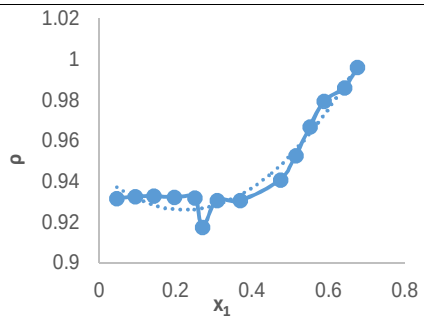

Fig.21. x_1 vs ρ

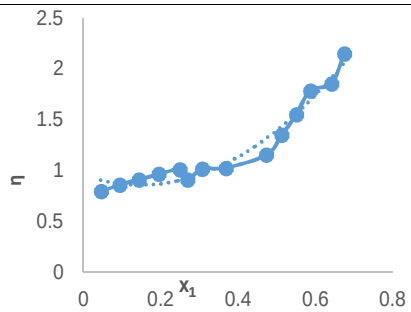

Fig.22. x_1 vs η

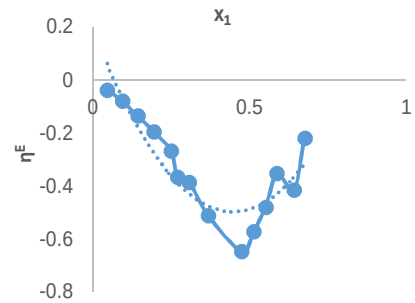

Fig.23. x_1 vs η^E

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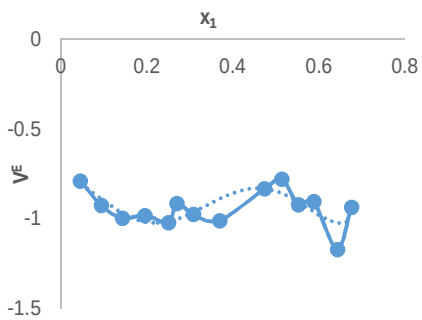

Fig.24. x_1 vs V^E

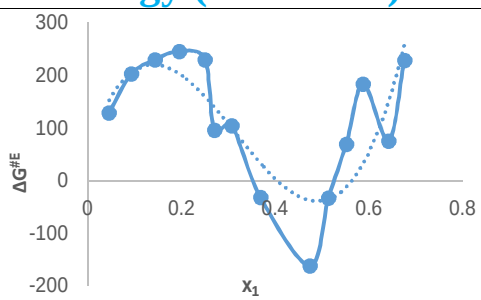

Fig.25. x_1 vs $\Delta G^{\#E}$

Plots for system - 6

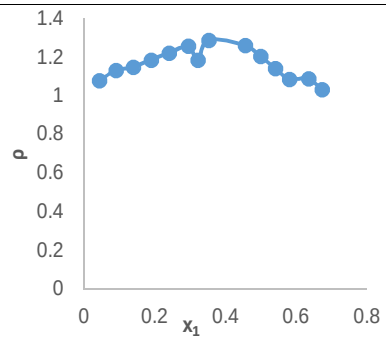

Fig.26. x_1 vs ρ

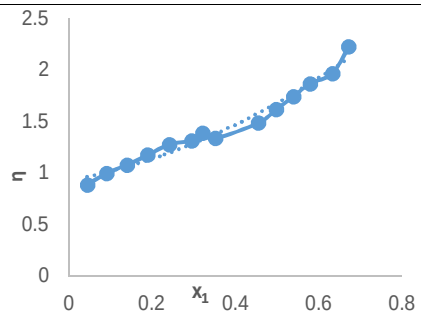

Fig.27. x_1 vs η

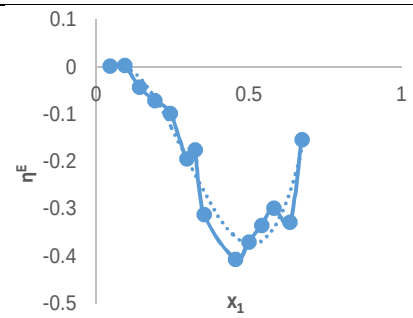

Fig.28. x_1 vs η^E

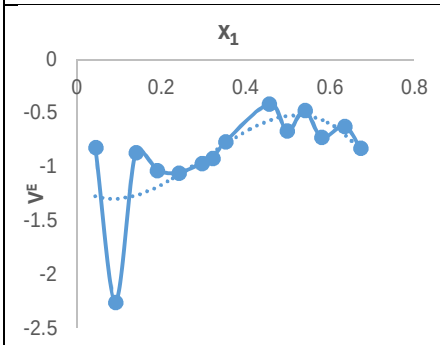

Fig.29. x_1 vs V^E

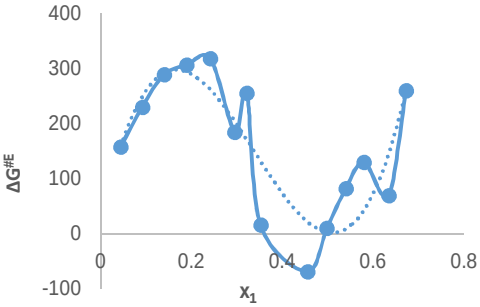

Fig.30. x_1 vs $\Delta G^{\#E}$

D. Interaction parameter (d)

A perusal of Table-1 shows that the values of ***d*** are negative over the entire range of composition in systems with MEK while positive in systems with N,N-DMF as a second component. Applying Grunberg and Nissan [19] equation to several binary systems, Nigam and Mahl [36] have concluded as below -

1) If $\eta^E > 0$, $d > 0$ and the magnitude of both is large, the strong specific interaction would be present.

2) If $\eta^E < 0$, $d < 0$, then weak specific interaction would be present, and

3) If $\eta^E < 0$, $d < 0$ and the magnitude of both is large, then specific interaction would be absent.

However, Oswal and co-workers [35], [37], [38] have asserted that the above conclusions of Nigam and Mahl [36] do not seem to be applicable to the liquid mixtures with components differing in size and suggested that the negative values of ***d*** indicate that dispersion forces are dominant [39]-[42], values becoming less negative and in some cases become positive as the strength of interactions increases.

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V. CONCLUSION

Molecular interactions are present in all six ternary systems of Aniline. Plots of densities and viscosities are nonlinear and the appearance of the curve is the clear indication of the structural changes in the pure components when they are mixed at various concentrations. Values of η^E are negative for all ternary mixtures over the entire range of composition. Values are more negative in systems – 1, 2 & 3 than those in systems – 4, 5 & 6 which indicates the more compact arrangement of unlike molecules in latter case due to possibility of hydrogen bond formation. The values of V^E are negative for all ternary systems over the entire range of composition. This may be attributed to the complex formation due to dipole and dipole-induced dipole interactions and interstitial rearrangement. The values of ($\Delta G^{\#E}$) and (*d*) are negative over the entire range of composition in systems containing MEK as the second component suggesting the dominance of dispersion forces. However, these values are positive in systems comprising N,N-DMF as a second component except at the lower concentration of second component where the values are negative, suggesting the presence of specific interactions. Hence, it can be concluded that though all ternary systems are showing the presence of molecular interaction, systems containing N,N-DMF as a second polar component are showing higher degree of specific interaction.

VI. ACKNOWLEDGEMENT

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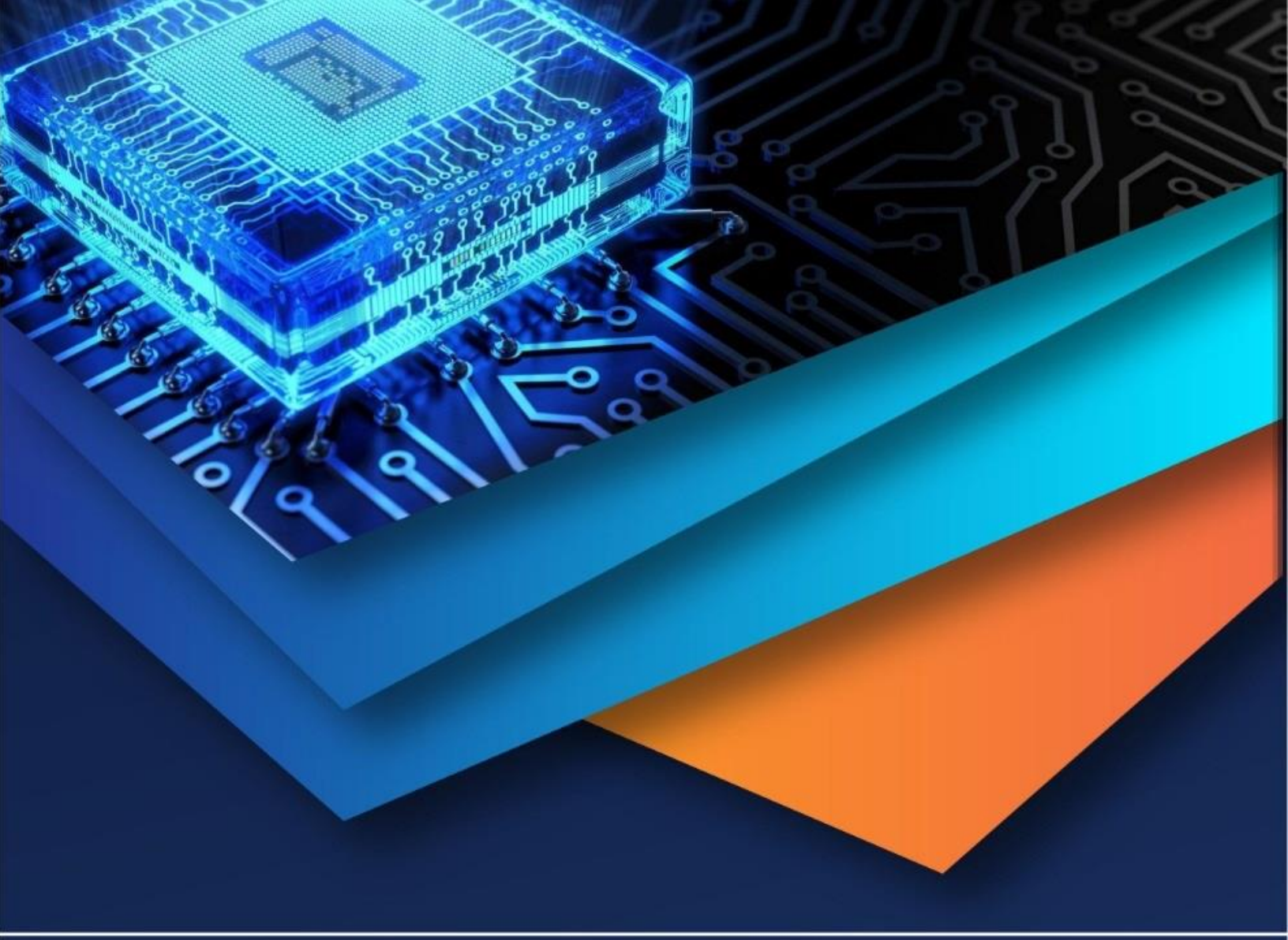

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