

# Solvation Analysis of Derivatives of Nitrones by Quantum Mechanical Method

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**Abstract— Solvation analysis of nitrones has been carried out by the polarizable continuum model (PCM). The electrostatic contribution of free energies of solvation of the compounds is discussed. The effects of dispersion energy, repulsion energy, cavities and dipole moments are examined. The test set consists of different polar and non-polar solvents of various range of dielectric constant. Quantum mechanical self-consistent fields explain the properties of compounds.**

**Keywords-** Solvation analysis, nitrones, electrostatic repulsion

## I. Introduction

Specific nitrones have been used for more than 30 years in analytical chemistry and biochemistry to trap and stabilize free radicals for the purpose of their identification and characterization. Within six years of the beginning of the use of nitrones in analytical chemistry, they were starting to be used in biochemical systems. Solvation analyses have been done for different nitrones such as nicotinic acid N-oxide, isonicotinic acid N-oxide, 8-Hydroxy quinoline, 2 picoline N-oxide and pyridine N-oxide.

## II. Experimental detail

### A. Methods of computation

Solubility studies of nitrones have been carried out for nicotinic acid n oxide, isonicotinic acid n oxide, 8 hydroxy quinoline, 2-picoline n oxide, pyridine n oxide. The geometries are obtained by using the molecular mechanics method. The molecules are solved by using the molecular mechanics method. The molecules are solved with solvents of various dielectric constants using a PCM by the Gaussian DFT method using the basis sets of cc-pVDZ to interpret the solvent effect of the molecules. The computer program Gaussian 03 was used for this purpose.

## III. Results and Discussion

### A. Electrostatic contributions in free energy

The solvation effects of nitrones are investigated. For this purpose, the free energy, electrostatic interaction, dispersion energy and repulsion energy of some nitrones in different solvents are evaluated by Polarized Continuum Model (PCM). These quantities typically converge quickly during a simulation and thus can provide a good assessment of the computational approaches in describing solvent-solute interaction [9]. A set of polar and non-polar solvents like water, methanol, ethanol, chloroform, methylene chloride, carbon tetrachloride, benzene, toluene, heptanes, cyclohexane, aniline, THF and DMSO were used for this solvation analysis (Table-1).

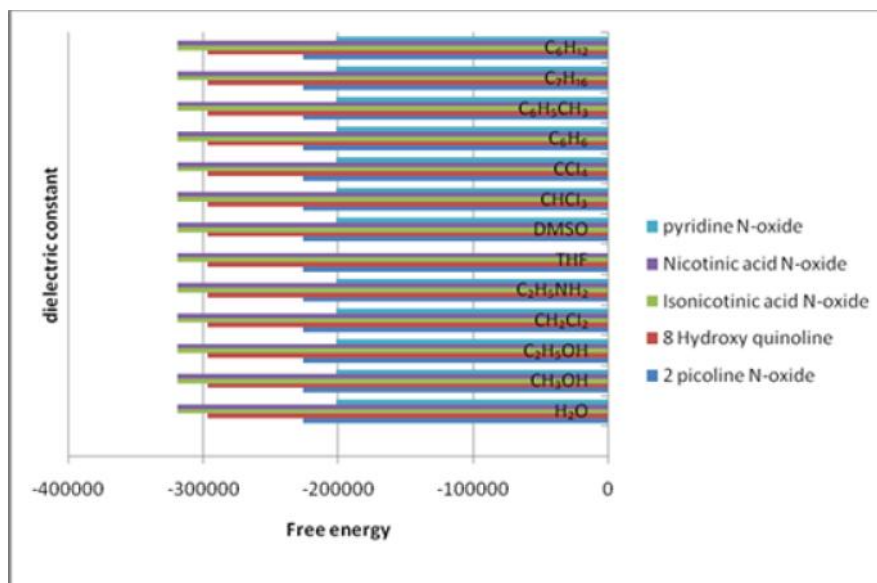


Fig. 1 dielectric constant vs free energy

**Table 1 Electrostatic interaction of solvation of nitrones in various Solvents (kJ/mole)**

Solvent	2 picoline N-oxide	8 Hydroxy quinoline	Isonicotinic acid N-oxide	Nicotinic acid N-oxide	pyridine N-oxide
Polar					
H <sub>2</sub> O	-15.18	-8.53	-19.83	-22.44	-16.77
CH <sub>3</sub> OH	-14.78	-8.32	-19.35	-21.88	-16.33
C <sub>2</sub> H <sub>5</sub> OH	-14.55	-8.21	-19.09	-21.56	-16.08
CH <sub>2</sub> Cl <sub>2</sub>	-13.03	-7.42	-17.26	-19.42	-14.41
C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	-12.36	-7.07	-16.44	-18.46	-13.66
THF	-12.62	-7.21	-16.76	-18.84	-13.95
DMSO	-14.98	-8.43	-19.6	-22.17	-16.56
Non Polar					
CHCl <sub>3</sub>	-11.2	-6.46	-15.02	-16.81	-12.38
CCl <sub>4</sub>	-6.98	-4.16	-9.64	-10.67	-7.7
C <sub>6</sub> H <sub>6</sub>	-7.04	-4.2	-9.72	-10.75	-7.77
C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	-7.43	-4.41	-10.22	-11.33	-8.2
C <sub>7</sub> H <sub>16</sub>		-3.55	-8.2	-9.05	-6.5
C <sub>6</sub> H <sub>12</sub>	-6.28	-3.77	-8.72	-9.54	-6.93

#### B. Dispersion energy

The dispersion energy is due to polarization of the solvent molecules by the solute molecule [17]. This polarization in turn may depend on dipole moment of the solvent molecule. From the data in table 4 it is found that dispersion energy is maximum for all molecules with chloroform.

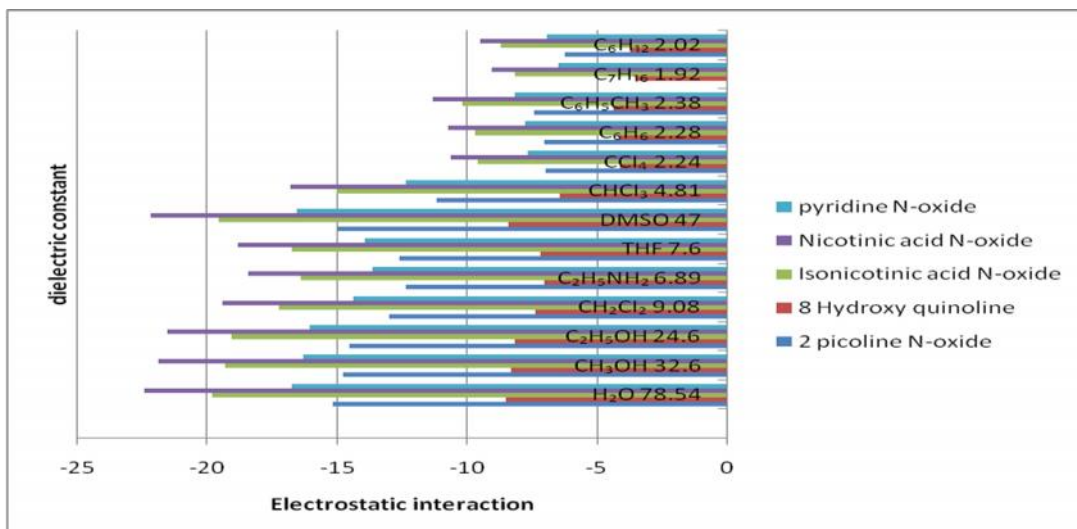


Fig. 2 Dielectric constant vs electrostatic interaction

Table 2 Dispersion energy of solvation of nitrones in various solvents (kJ/mole)

Solvent	2 picoline N-oxide	8 Hydroxy quinoline	Isonicotinic acid N-oxide	Nicotinic acid N-oxide	pyridine N-oxide
Polar					
H <sub>2</sub> O	-12.56	-16.36	-14.89	-14.88	-11.91
CH <sub>3</sub> OH	-10.83	-14.1	-12.83	-12.82	-10.27
C <sub>2</sub> H <sub>5</sub> OH	-11.08	-14.42	-13.12	-13.11	-10.5
CH <sub>2</sub> Cl <sub>2</sub>	-10.64	-13.76	-12.51	-12.49	-10.04
C <sub>2</sub> H <sub>5</sub> NH <sub>2</sub>	-13.52	-17.59	-16.01	-15.99	-12.81
THF	-11.78	-15.32	-13.93	-13.92	-11.16
DMSO	-12.94	-16.8	-15.28	-15.26	-12.24
Non polar					
CHCl <sub>3</sub>	-9.62	-12.43	-11.29	-11.27	-9.07
CCl <sub>4</sub>	-9.76	-12.6	-11.44	-11.42	-9.19
C <sub>6</sub> H <sub>6</sub>	-11.99	-15.61	-14.2	-14.19	-11.37
C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	-12.23	-15.92	-14.49	-14.47	-11.59
C <sub>7</sub> H <sub>16</sub>	-10.82	-14.08	-12.81	-12.79	-10.25
C <sub>6</sub> H <sub>12</sub>	-11.68	-15.19	-13.82	-13.81	-11.06

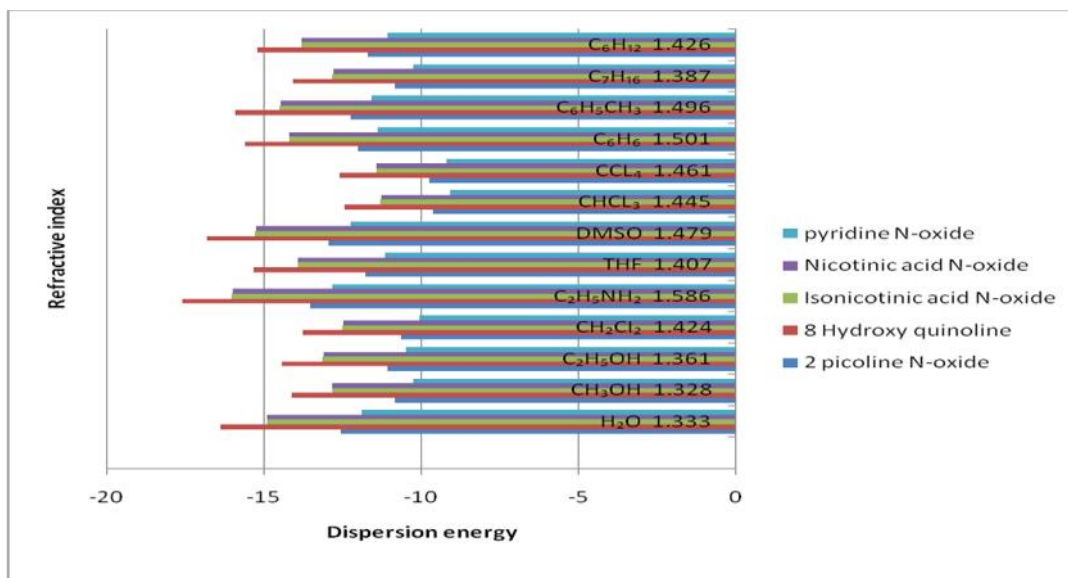


Fig. 3 refractive index vs dispersion energy

C. Repulsion energy

The repulsion energy varies for one solvent to another. This value also indicates that the dielectric constant as well as molecular size of the solvent molecules determines the repulsive energies. This is supported by the higher values of the repulsive energies of the nitrone in aniline except for 2-picoline n oxide. It may be noted that repulsion energy is lesser in chloroform when compared to other solvent. This may be due to polarizability effect of solvent and attached methyl groups in the solute. By relating in refractive index of solvents with repulsion energy, there are uniform changes except in the chloroform. This may be due to more hydrogen an atom present in the interaction .Plot of refractive index vs. repulsion energy is shown in fig 4.

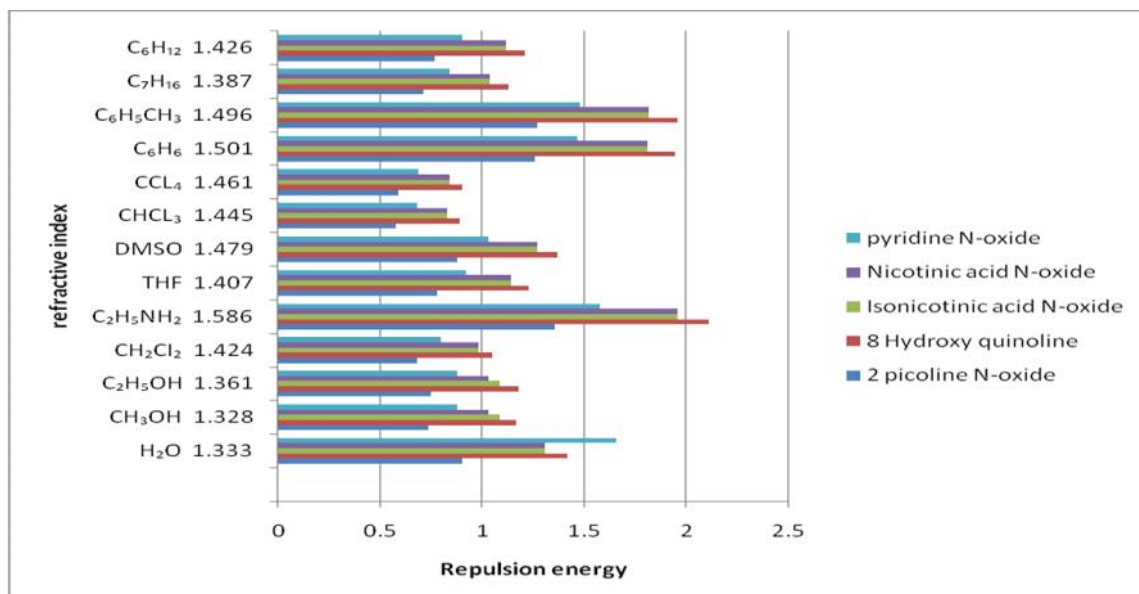


Fig. 4 Refractive index vs Repulsion energy

#### D. Contribution of cavitation enthalpies

The cavitation enthalpies obtained in the present calculations are expected to have reasonable accuracy based on the formulas given by Sinangolu and Pierotti. These formulas obtained from experimental solubility have allowed to check the adequacy of the scaled particle theory to calculate free energy [13, 14]. Cavitation enthalpies of nitrones in different solutions are the measure of enthalpy contribution to the free energy of solvation. The computed values of two different methods by Sinangolu and Pierotti are presented in Table 7. The cavitation enthalpies calculated by two methods give two different results. However the trend is similar. Among polar solvents, the cavitation enthalpy has the highest positive values for all the six systems in DMSO by pierotti method and has negative values in Sinangolu method and in aprotic solvents cavitation enthalpy has highest positive value in benzene.

Table 4 Cavitation enthalpies for different solvents in (kcal/mol)

Solvent	2 picoline N-oxide		8 Hydroxy quinoline		Isonicotinic acid N-oxide		Nicotinic acid N-oxide		pyridine N-oxide	
	pierotti	sinangolu	pierotti	sinangolu	pierotti	sinangolu	pierotti	sinangolu	pierotti	sinangolu
Polar										
H <sub>2</sub> O	2.34	23.777	2.1059	26.889	2.485	25.302	2.51	25.56	2.049	20.736
CH <sub>3</sub> OH	7.719	10.433	6.961	36.123	8.188	10.996	8.267	11.092	6.78	9.308
C <sub>2</sub> H <sub>5</sub> OH	8.051	10.297	9.044	11.44	8.538	10.857	8.621	1.0952	24.719	9.18
CH <sub>2</sub> Cl <sub>2</sub>	10.255	2.076	11.519	2.615	10.875	2.34	10.98	2.385	9.013	1.549
C <sub>2</sub> H <sub>5</sub> NH <sub>2</sub>	16.283	12.934	18.338	14.746	17.291	13.822	17.462	13.972	14.266	11.164
THF	116.119	0.926	104.081	1.479	123.582	1.197	124.84	1.243	-	-
DMSO	1139.43	-70.204	1281.54	-91.703	1209.18	-80.743	1220.95	-82.524	999.794	-49.194
Non Polar										
CHCl <sub>3</sub>	9.416	1.718	10.572	2.257	9.983	1.982	10.079	2.027	8.28	1.19
CCl <sub>4</sub>	10.547	8.514	11.842	10.062	11.183	8.273	11.29	9.401	9.274	7.002
C <sub>6</sub> H <sub>6</sub>	12.965	9.344	14.565	11.02	13.75	10.165	13.883	10.304	11.392	7.706
C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	10.272	9.195	11.537	10.841	10.893	10.002	10.998	10.138	9.029	7.585
C <sub>7</sub> H <sub>16</sub>	-	-	10.457	7.565	9.881	6.947	9.975	7.048	8.213	5.17
C <sub>6</sub> H <sub>12</sub>	10.359	7.779	11.63	9.251	10.983	8.5	11.088	8.622	9.11	6.34

#### IV. Conclusion

The success of Polarizable Continuum model of calculation depends on ability of the model to approximate the system under consideration. The Polarizable Continuum models are reasonable compromise between accuracy, generality and flexibility. The errors in the solute free energy calculated in this method are considerable less. The limitations arise from the fact that Polarizable Continuum model is basically an empirical method. Therefore, it is applicable to compounds where adequate experimental data are available. Thus one can calculate the geometry of wide range of molecules satisfactorily using Polarizable Continuum model. The quantum mechanical solvation analyses have been carried out for different nitrones. The computed physical properties such as free energy components, electrostatic interaction, and dipole moments are discussed. The interaction between the five nitrones and various solvents are investigated.

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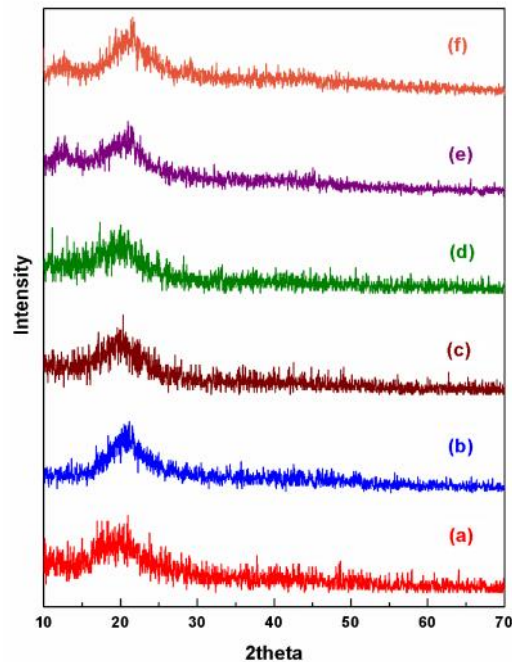
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**Figure 1.** FT-IR spectra of (a) 0 wt % NiO (b) 0.1 wt% NiO (c) 0.2 wt% NiO (d) 0.3 wt% NiO (e) 0.4 wt% NiO (f) 0.5 wt% NiO.

### B. X-Ray Diffraction Analysis

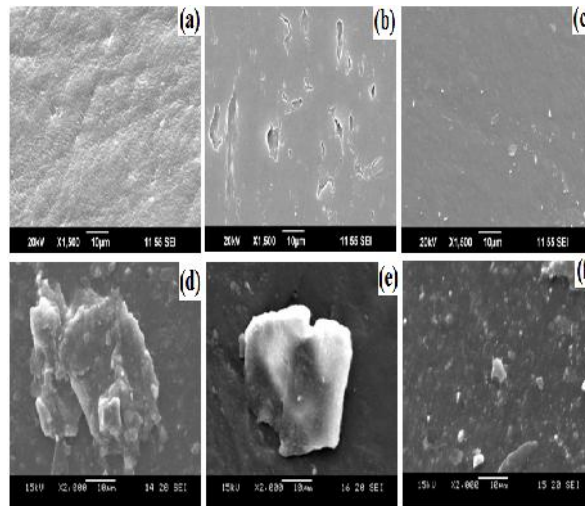
The XRD pattern of NiO nanoparticle filled PU-DIOL/PCL blend is given in figures (a)-(f). The diffracted intensities were recorded from  $10^\circ$  to  $70^\circ$ . Figures (a-d) show a predominant and broad peak with a maximum at  $2\theta = 19.8, 20, 19.96$  which corresponds to the polymer blend. Figures (e, f) show two peaks at  $2\theta = 20.28, 12.92$  and  $2\theta = 21.16, 12.12$  which correspond to the polymer blend and NiO composite. This broad peak indicates the amorphous nature of the polymer.



**Figure.2.** XRD pattern of NiO nanoparticle filled PU-DIOL/PCL blend (a) 0 wt % NiO (b) 0.1 wt% NiO (c) 0.2 wt% NiO (d) 0.3 wt% NiO (e) 0.4 wt% NiO (f) 0.5 wt% NiO.

### C. Scanning Electron Microscopy Analysis

SEM showed how the microspheres are inserted in the fine-grained organic matrix. The SEM images of composites are shown in the Fig.3.(a-f)



**Figure.3.** SEM images for(a)0 wt % NiO (b) 0.1wt%NiO (c)0.2wt%NiO (d) 0.3wt% NiO(e) 0.4wt%NiO (f) 0.5wt%NiO.

#### D. Samples treatment

1. Water absorption test according to the ASTM D570 was conducted on PU-DIOL/PCL-NiO by immersing the specimen in distilled water at room temperature for 35 days. The weight gained at any time  $t$ ,  $M_t$  as a result of water absorption was determined using the equation.

$$\text{Water absorption, } M_t = ((W_w - W_d) / W_d) \times 100$$

Where  $W_d$  and  $W_w$  represent the material dry weight and weight of materials after being exposed to the water absorption at a period of time,  $t$  respectively.

2. Swelling studies were carried out by immersing the test specimens in specific solvents for 25 days with periodical weighing after removal of the excess solvent from the sample using filter paper. This was repeated until constant weight (equilibrium swelling). The swelling degree,  $q$ , was calculated using gravimetric method using the equation

$$q = (m - m_0) / m_0$$

Where  $m$  and  $m_0$  are the sample weights after and before swelling, respectively [12].

#### E. Water absorption

Moisture absorption is attributed to the presence of free volume and hydrophilic functional groups such as hydroxyl groups in their backbone structure. In Figure.1, the results show that PU-DIOL/PCL blend has increased water absorption property along with nano composites such as Blend + 0.1%NP, Blend + 0.3%NP, Blend+0.4%NP. However, it is clearly observed that the blend absorbs less water.

When compared to nano composite blends. The Blend+0.5%NP exhibited higher percentage of water absorption than the other because of the percentage of NiO has been increased. The blend, as well as nano composite blends have polymers with high electronegative atoms and therefore dipolar groups favouring the interaction between water and the synthesized materials and hence water absorption takes place.



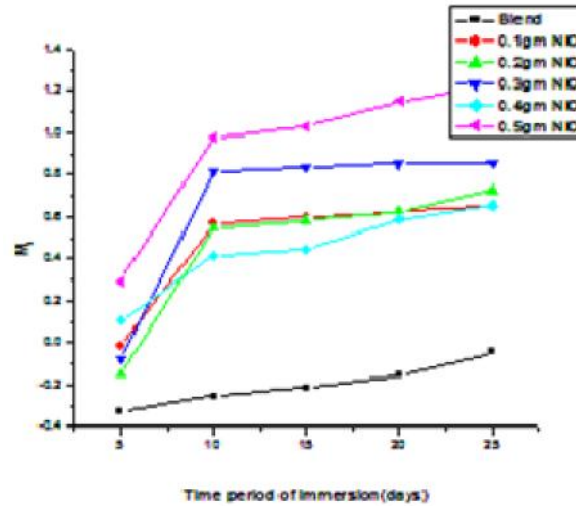


Figure .4. Water absorption of composites

#### F. Solubility of polymer composites

The blend and the composites are immersed in Dimethyl formamide, Dimethyl sulphoxide, Ethyl methyl ketone. The polymer composites are completely dissolved in the solvents. This is due to the high polarity interaction between the synthesized material and solvents mentioned. The blend and the polymer nano composites are partially soluble in solvents like Ethanol, Diethyl ether, Ethyl acetate, given Table 1.

TABLE.1. SOLUBILITY OF POLYMER COMPOSITES

Code	Solubility							
	wate r	etha nol	IN Hc l	IN Na O H	D M S O	D M F	E A	E M K
Blend	∅	⊗	∅	∅	×	×	⊗	×
Blend+0.1%N	∅	⊗	∅	∅	×	×	⊗	×
Blend+0.2%N	∅	⊗	∅	∅	×	×	⊗	×
Blend+0.3%N	∅	⊗	∅	∅	×	×	⊗	×
Blend+0.4%N	∅	⊗	∅	∅	×	×	⊗	×
Blend+0.5%N	∅	⊗	∅	∅	×	×	⊗	×

⊗ - Partially soluble, ∅ - Insoluble, × - Soluble

#### G. Swelling studies

However the solvents such as HCl, NaOH were absorbed by the blends and nano composite blends. 'q' is observed because of the extraction of the sol fraction in the synthesized material through the electrostatic attraction. The absorption of the different solvents is depicted in the plots given below

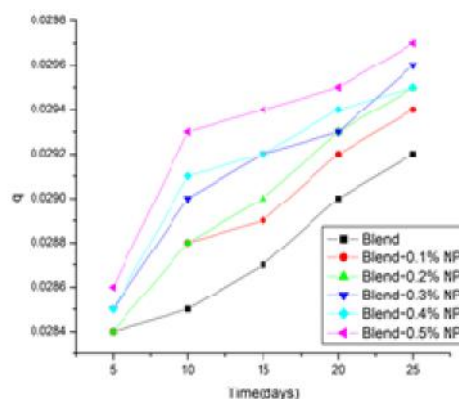


Figure 5. Swelling property of PU-DIOL/PCL-NiO nanocomposites in 1N HCL

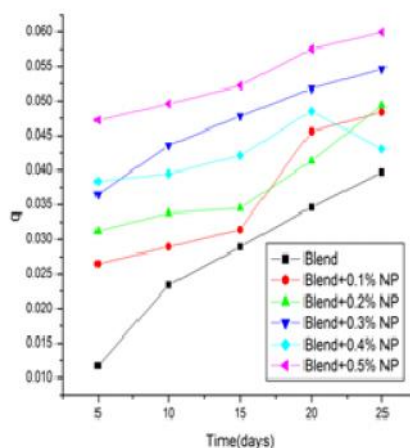


Figure 6. Swelling property of PU-DIOL/PCL – NiO Nanocomposites in 1N NaOH

#### IV CONCLUSION

Polymer composites with NiO of varying composition were prepared. The composites are immersed in Dimethyl formamide, Dimethyl sulphoxide, Ethyl methyl ketone. The polymer composites are completely dissolved in these solvents. This is due to the high polarity interaction between the synthesized material and solvents mentioned. The polymer composites are partially soluble in solvents like Ethanol, Diethyl ether, Ethyl acetate.

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