CHAPTER V
RESULTS & DISCUSSIONS

5.1 Model Development and Validation

The models developed in past by Muro-Suñé (2002) describe the scenarios with and without surfactant effect and also the effect of pesticide and surfactant diffusing together on the uptake of pesticide. The results were encouraging and need to be improved further to take more factors into account, such as the droplet evaporation and the dependence of solubility of pesticide in plant on concentration of surfactants. Rasmussen (2003) developed model for the uptake of lipophillic pesticides into the leaf cuticle.

Lipophilic adjuvants are thought to work by plasticization of the surface leaf wax layer on the plant. The rate of diffusion of the adjuvant in the leaf wax is dependent on the concentration of the adjuvant. Conventionally, experiments have measured the diffusion coefficient of the pesticide individually or in the presence of adjuvants. At saturation concentration the rate of diffusion is measured for linear alkane ethoxylates in barley wax (Burghardt et al., 1998). There are, however no such data where the diffusion coefficient is accounted as a result of systematic change in adjuvant concentration.

The above model was used by Rasmussen (2003) in order to remedy this lack of data, where he regressed some experimental data from work where several adjuvant concentrations had been used [Stock et al.,1993]. The linear dependence between the diffusion coefficient and adjuvant concentration was assumed and the results was fitted for cyanazine with the adjuvants (alkane ethoxylates) C13E6, C13E11, C13E15 and C13E20, each being used at three different concentrations. The results where excellent for pesticide alone or with C13E6 but the model could not explain the concentration dependence for longer chain ethoxylates. This proves that there is another mechanism operating between the long chain ethoxylates and possibly with other short chain ethoxylates, which has not been modeled.

The other drawback of the model is the requirement of lots of parameters, which are usually not known and therefore must be estimated in order to make the

model work. On the other hand the large number of parameters requires a large amount of experimental data and makes the model too much dependent on correlations of limited application.

The scope of this work is to develop mathematical models and investigate their ability to produce realistic results. Several versions of models were developed and tested in order to come close to reality .The changes were made in estimation of parameters such as diffusion coefficients and solubility of pesticides in surfactants. This section focuses on step-by-step development and validation of model from first version to the final version.

All the models were tested for uptake of cyanazine on wheat plant. The cyanazine was added with a concentration of 0.5g/l. Four different linear alkane ethoxylates (C13E6, C13E11, C13E15, C13E20) having different ethoxy chain length where chosen to be combined with Cyanazine. Each surfactant was used in three different concentration of 0.2,1 and 5 g/l. The common parameters needed in the models were obtained from database described in section 2.1 and are given in table 5.1.

Table 5.1 Common Parameters

Common Parameters	Value
Thickness of Wax compartment, X_{wax}	2.00E-07 m
Thickness of Cuticle compartment, X_{cut}	1.80E-06 m
Initial volume of Droplet, V0	2.00E-10 m^3
Volume of plant, Vp	1.00E-06 m^3
Surface factor, sf	1
Volume Factor, vf	1
Final time of Evaporation, tf	1 h

The other parameters were estimated using the Model preparation tools described in section 2.2. The values obtained for the parameters of cyanazine that are needed in these models are given below in table 5.2:

Table 5.2 Estimated Parameter values for Cyanazine needed in the model

Active Ingredient	Cyanazine
KwdAI (Wax/Water)	12.58925
KcpAI (Cuticle/Plant)	19.40886
KwcAI (Wax/Cuticle)	0.648634
McGowan Volume (cm^3/mol)	177.43

Since a new solubility correlation has been introduced which takes into account the change of solubility of pesticide in droplet due to change in surfactant concentration, therefore the initial concentration of pesticide in droplet will no longer be same as calculated in section (2.2). The solubility of the pesticide in the water droplet will now be estimated from its solubility in water, its solubility in pure adjuvants and their compositional ratio. The solubility of some pesticide in the C13 adjuvants given in table 5.3 has been estimated in the literature and has been extracted.

Table 5.3 Estimated Solubility of Cyanazine in Water and ethoxy- surfactants

Pesticide	Water (g/l)	C13E6 (g/l)	C13E11 (g/l)	C13E15 (g/l)	C13E20 (g/l)
Cyanazine	0.17	56.4	70.4	78.4	84.4

It was assumed that the solubility of the pesticide will depend on the volume fraction of surfactant and water present in the droplet therefore correlation given in equation (5.1) was proposed in order to calculate the solubility.

$$S_{droplet} = S_{water} * vfr_{water} + S_{adj} * vfr_{adj} \quad (5.1)$$

$S_{droplet}$ is the solubility of cyanazine in water droplet (g/l).

S_{water} is the solubility of cyanazine in water (g/l).

S_{adj} is the solubility of cyanazine in surfactant (g/l).

vfr_{adj} is the volume fraction of surfactant in the droplet.

$vfr_{water} = 1 - vfr_{adj}$, is the volume fraction of water in the droplet.

The calculated values of initial concentration of cyanazine in water droplet in presence of different surfactants are given in table 5.4 below;

Table 5.4 Calculated initial concentrations of Cyanazine in droplet

Surfactant (g/l)	CdAl0 (mol/m3)	MAltotal (mol)	MAl0 (mol)
C13E6			
0.2	0.46354	4.17E-10	3.24E-10
1	0.57712	4.17E-10	3.01E-10
5	1.15089	4.17E-10	1.86E-10
C13E11			
0.2	0.47018	4.17E-10	3.23E-10
1	0.61177	4.17E-10	2.94E-10
5	1.31974	4.17E-10	1.53E-10
C13E15			
0.2	0.48094	4.17E-10	3.20E-10
1	0.66557	4.17E-10	2.84E-10
5	1.58871	4.17E-10	9.89E-11
C13E20			
0.2	0.47787	4.17E-10	3.21E-10
1	0.6502	4.17E-10	2.87E-10
5	1.51189	4.17E-10	1.14E-10

Similarly the parameters were estimated for each of the surfactant to be used in these models. There estimated values are obtained from database described in section (2.1) and are given below and shown in table 5.5.

Table 5.5 Partition coefficients for surfactants

Surfactants	Kwdadj	Kcpadj	Kwcadj
C13E6	851.138038	9120.108394	0.0933254
C13E11	60.2559586	1318.256739	0.0457088
C13E15	7.2443596	288.4031503	0.0251189
C13E20	0.51286138	41.68693835	0.0123027

Table 5.6 McGowan Volume for surfactants

Surfactants	McGowan Volume (cm^3/mol)
C13E6	404.2
C13E11	574.45
C13E15	710.65
C13E20	880.9

Table 5.7 Calculated initial concentrations for surfactants

Surfactants	Surfactant Rate (g/l)	C_{dadj0} (mol/m^3)	$M_{adjtotal}$ (mol)	M_{adj0} (mol)
C13E6	0.2	0.0187	8.62069e-11	8.24669e-11
	1	0.0187	4.31034e-10	4.27294e-10
	5	0.0187	2.15517e-09	2.15143e-09
C13E11	0.2	0.0527	5.84795e-11	4.79395e-11
	1	0.0527	2.92398e-10	2.81858e-10
	5	0.0527	1.46199e-09	1.45145e-09
C13E15	0.2	0.1207	4.65116e-11	2.23716e-11
	1	0.1207	2.32558e-10	2.08418e-10
	5	0.1207	1.16279e-09	1.13865e-09
C13E20	0.2	0.18518519	3.70370e-11	0
	1	0.3405	1.85185e-10	1.17085e-10
	5	0.3405	9.25926e-10	8.57826e-10

Table 5.8 shows the estimated contact angles and surface area of some of surfactants

Surfactant	Contact Angles (degrees)	Droplet surface area, S0 (m^2)
C13E6	30-70	1.31e-06
C13E11	90	6.56e-07
C13E15	105	4.92e-07
C13E20	120	3.28e-07
None	0	1.59e-07

The values of parameters obtained above were mostly common in new version of models only the difference was in terms of estimation of diffusion coefficient. In the next section each of the models were simulated using various correlation for diffusivity and the results were compared with the experimental data taken from Stock *et.al* (1993) as well as with simulated results obtained by Rasmussen (2003).

5.2 Uptake Models

5.2.1 Version 1

The work done in the past was not able to account for the solubilisation of the pesticide into the water droplet by the adjuvant. This model takes into account the solubility correlation developed in section (2.2.2a). The model also contains the evaporation droplet model but it is assumed that no significant spreading or evaporation will occur after the droplet has been applied (Bell, 2003) so the surface area and the volume are set constant.

The diffusivity correlation used in this model was similar to one used by Rasmussen (2003) which is as follows,

$$D_{AI,i} = (D_{i,wax} + k_1.C_{adj,i}).\exp(-(beta_{i,wax} + k_2.C_{adj,i}).MV_{AI}) \quad (5.2)$$

$$D_{AI,j} = (D_{j,cut} + k_3.C_{adj,j}).\exp(-(beta_{j,cut} + k_4.C_{adj,j}).MV_{AI}) \quad (5.3)$$

$$D_{adj,i} = (D_{i,wax} + k_5.C_{adj,i}).\exp(-(beta_{i,wax} + k_6.C_{adj,i}).MV_{adj}) \quad (5.4)$$

$$D_{adj,j} = (D_{j,cut} + k_7.C_{adj,j}).\exp(-(beta_{j,cut} + k_8.C_{adj,j}).MV_{adj}) \quad (5.5)$$

Where;

i refers to wax layers (i=0,1,2……..15^{th} layer of wax).

j refers to cuticle layers(j=16,17,18……..30^{th} layer of cuticle).

$C_{adj,i}$ and $C_{adj,j}$ are adjuvant concentrations in wax and cuticle layers respectively.

MV_{adj}, MV_{AI} are McGowan Volumes of adjuvant and active ingredient respectively.

$D_{i,wax}$, $D_{j,cut}$ are diffusion coefficients for a theoretical molecule with no volume for wax and cuticle layers respectively.

$beta_{i,wax}$, $beta_{j,cut}$ are the size selectivity or reciprocal of free volume available for diffusion for wax and cuticle layers respectively.

k1 –k8 aie arbitrary parameters.

The additional parameters needed in the above diffusivity correlation were taken from work done by Rasmussen (2) and they are provided in table 5.9.

Table 5.9 Additional parameter values for Diffusivity correlations

Parameter	Value
$D_{0,wax}$	5.4954e-16 m2/s
$D_{0,cut}$	1.0e-13 m2/s
$\beta_{0,wax}$	0.0230 mol/cm3
$\beta_{0,cut}$	0.0230 mol/cm3
k1	1.73e-17
k2	-0.00066
k3	3.15e-15
k4	-0.00066
k5	1.73e-17
k6	-0.00066
k7	3.15e-15
k8	-0.00066

Simulations have been carried out for each of surfactant and pesticide combinations using the above additional parameters. The results were compared with experimental data as well as with the old model E2 used by Rasmussen (2003).

Figure 5.1 given below shows the comparison of all the three results for Cyanazine uptake at 24 hours.

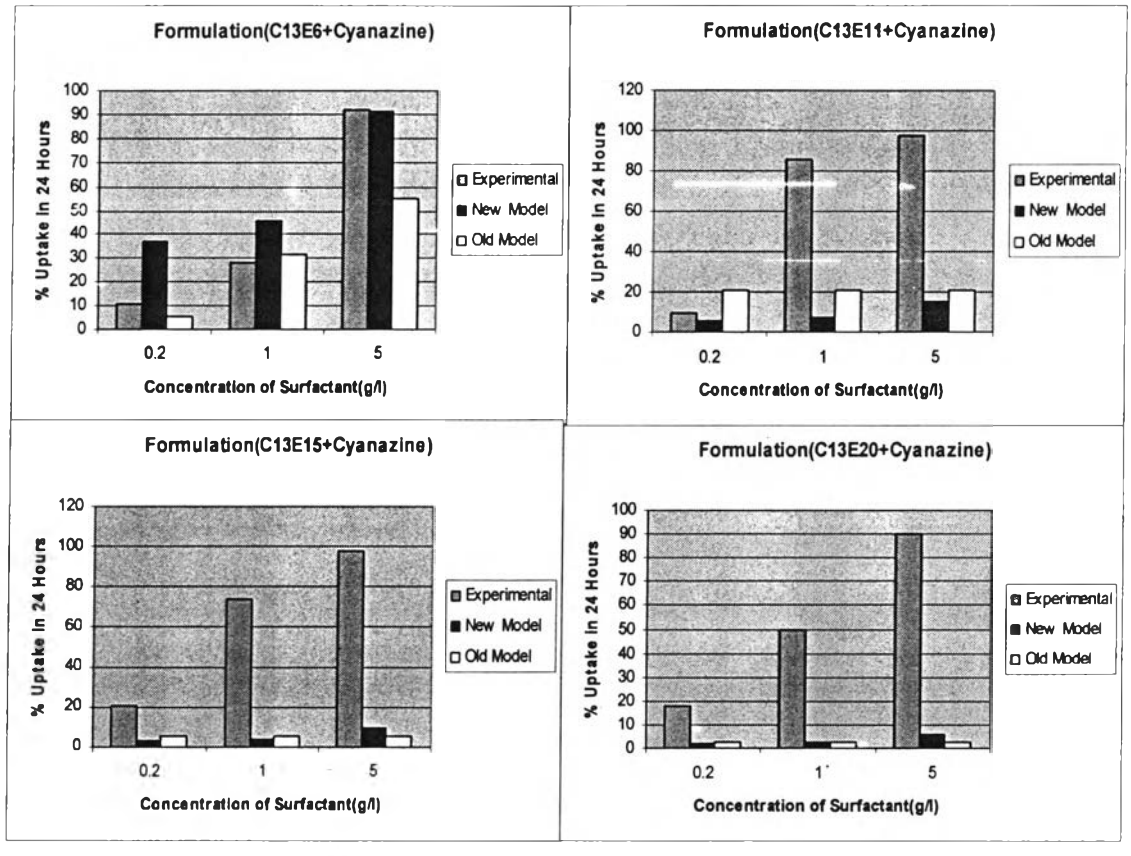

Figure 5.1 Comparison of results for uptake of cyanazine at 24 hours.

It can bee seen that results obtained were good for surfactant C13E6 but couldn't able to give good results for surfactants of longer ethoxy chain length. The simulation also predicts that the uptake of cyanazine with C13E20 is much lower when cyanazine is used with C13E6.This is because of smaller surface area of droplet with C13E20, which is a very sensitive parameter in the model.

As compared to old model E2 (Rasmussen, 2003), the results showed higher variation in uptake values with change in concentration of surfactant, which cannot be seen, in the old model E2 (Rasmussen, 2003). Therefore it was encouraging to further modify the new model in order to come close to the real scenario.

5.2.2 Version 2

The major drawback with the above model was that the numbers of parameters were quite high and also parameters k1 through k8 are generally not known so some sort of relationship between them must be assumed in order to fit parameters to that model. Even the results obtained were not promising although they showed variation in uptake with change in surfactant concentration, which can also be seen, in the experimental results. Therefore a new diffusivity correlation has to be proposed in order to update the model.

After the careful examination of literature (Burghardt *et al.*, 1998) the diffusivity correlations (5.6) and (5.7) were estimated by Bell (2004), which replaced the above equations (5.2), (5.3), (5.4) and (5.5) in version 2 of uptake model.

$$\log D_{adj} = -14.058 - 0.01.MV_{adj} \tag{5.6}$$

$$\log D_{AI} = -16.449 - 0.00227.MV_{AI} + 0.1266.\left(\frac{C_{adj}.MWadj}{rhow}\right) \tag{5.7}$$

Where;

D_{adj} and D_{AI} are diffusivity equations for surfactant and pesticide respectively

MV_{adj}, MV_{AI} are McGowan Volumes of surfactant and pesticide respectively.

C_{adj} is concentration of surfactant.

MW_{adj} is molecular weight of surfactant and rhow is density of wax.

There was no separate correlation used for wax and cuticle layers as it was assumed that diffusion of both pesticide and surfactants would not change much in both compartments.

The results obtained with the new diffusivity correlation can be seen and compared with the version1 and experimental results table 5.10.

Table 5.10 Comparison of results of Version 1 and Version 2 with Experimental data

Formulation	Surfactant Conc. (g/L)	Exp. Uptake %	Version 1 Predicted Uptake%	Version 2 Predicted Uptake%
Cyanazine	0	6	0.76631	0.36353
Cyanazine +C13E6	0.2	11	36.76034	40.42241
Cyanazine +C13E6	1	28	45.76685	50.32623
Cyanazine +C13E6	5	92	91.26882	99.59506
Cyanazine +C13E11	0.2	10	5.5195	3.02613
Cyanazine +C13E11	1	86	7.18167	3.93746
Cyanazine +C13E11	5	98	15.49252	8.494
Cyanazine +C13E15	0.2	21	3.02131	1.60229
Cyanazine +C13E15	1	74	4.18117	2.2174
Cyanazine +C13E15	5	98	9.98046	5.29294
Cyanazine +C13E20	0.2	18	1.78317	0.84926
Cyanazine +C13E20	1	50	2.45511	1.18489
Cyanazine +C13E20	5	90	5.70877	2.75516

It can been seen that the version 2 of the uptake model gave approximately same results as the previous eight-parameter model (version 1) and have to be modified in order to get more closer uptake values for surfactant of higher ethoxy chain length when compared to experimental uptake. The encouraging thing with new diffusivity correlations is that they do not contain too many parameters, which are difficult to obtain and fit in the model.

5.2.3 Version 3

The new equations (5.6) and (5.7) as proposed by Bell (2004) was more generalized to obtain the following five-parameter (K1, K2...K5) equations.

$$\log D_{adj} = K1 - K2.MV_{adj} \tag{5.8}$$

$$\log D_{Al} = K3 - K4.MV_{Al} + K5.\left(\frac{C_{adj}.MWadj}{rhow}\right) \tag{5.9}$$

Where K1 through K5 are parameters whose values have to be estimated in order to get near to real scenario. The sensitivity analysis was done in order to obtain the most sensitive parameter and can be seen from figure 5.2 below that K3 is highly sensitive parameter.

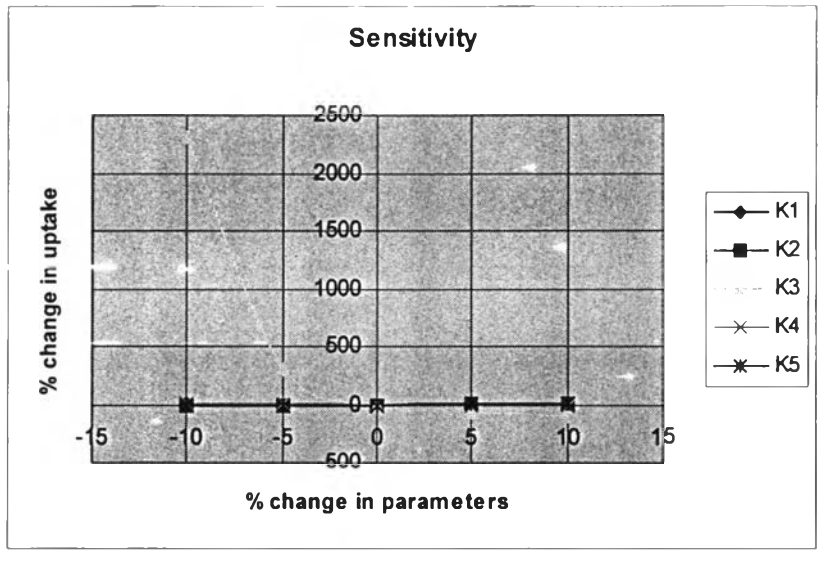

Figure 5.2 Sensitivity Analysis of Diffusivity Correlations

By trial and error method it is found that the K3 parameters, which fit the experimental values for Cyanazine Uptake, are given below in table 5.11,

Table 5.11 Fitted values of K3 for Uptake of Cyanazine at 24h and 120h.

Cyanazine		24 hours			120 hours		
Surfactant Conc.(g/L)	Surfactants	Exp. Uptake %	Predicted Uptake%	K3	Exp. Uptake %	Predicted Uptake%	K3
0.2	C13E6	11	11.01105	-17.23	16	16.18868	-17.85
	C13E11	10	9.94538	-15.73	13	13.13664	-16.29
	C13E15	21	21.11301	-15.04	23	23.02797	-15.7
	C13E20	18	18.06216	-14.86	19	19.06389	-15.535
1	C13E6	28	28.86172	-16.79	36	36.26028	-17.57
	C13E11	86	86.25058	-14.847	87	87.16284	-15.541
	C13E15	74	73.54735	-14.63	78	78.37408	-15.301
	C13E20	50	49.71294	-14.56	60	60.88567	-15.17
5	C13E6	92	92.23879	-16.5	96	96.34738	-17.432
	C13E11	98	97.8483	-15.135	99	99.07722	-15.828
	C13E15	98	97.54063	-14.89	99	99.0805	-15.582
	C13E20	90	90.02754	-14.67	98	98.1317	-15.331
0	None	6	6.02102	-15.3	12	12.01602	-15.67

It was seen from the above result that although different K3 values were able to fit the experimental data but no general trend was observed in these values. Physically K3 is very important parameter as it represents the tortuosity factor. Tortuosity is the ratio between the length of the path the pesticide needs to travel through the layer and the thickness of the layer. Since the thickness of each layer is constant therefore tortuosity is directly proportional to length of path pesticide needs to travel that is higher the K3 values longer will be the path and therefore lesser will be the uptake. For C13E6 the K3 values are according to expectation that is K3 values are smaller than the values obtained when no surfactant are used that is surfactant is helping in increasing the uptake of cyanazine but this is not the case with longer ethoxy chain surfactants like C13E15 and C13E20.Therefore model needs to be updated in order to predict results for all scenarios.

5.2.4 Final Version

The diffusivity correlation used in version 3 of uptake model was not different for wax and cuticle layer instead one equation each for active ingredient and surfactant was used in the model but in reality wax and cuticle are two separate layers where wax layer is the one which causes major hindrance in diffusion whereas diffusion through cuticle is much more easier. Therefore two different correlations were needed for both active ingredient and adjuvant, Data collected from the literature has been used to develop special correlations for diffusivity coefficients. The following final models (Bell, 2004) have been analyzed.

$$\log D_{AI,wax} = -16.449 - 0.00227 * MV_{AI} + 0.1266 * C_{adj} \quad (5.10)$$

$$\log D_{AI,cutin} = -13 - 0.01 * MV_{AI} \quad (5.11)$$

$$\log D_{adj,wax} = -13.02 + 0.01363 * C_{adj} - 0.01398 * MV_{adj} \quad (5.12)$$

$$\log D_{adj,cutin} = -10.23 - 0.015 * MV_{adj} \quad (5.13)$$

Where;

D_{adj} and D_{AI} are diffusivity for surfactant and pesticide respectively in wax and cutin.

MV_{adj}, MV_{AI} are McGowan Volumes of surfactant and pesticide respectively.

C_{adj} is concentration of surfactant.

Earlier the solubility of the pesticide in the water droplet was estimated from pesticide's solubility in water, its solubility in pure adjuvants and their compositional

ratio but experimental work done at Syngenta gave quite different results. Experimental results for the analysis of cyanazine in surfactant solution showed that the length of the ethoxylate chain does not seem to matter. After careful analysis following correlation was proposed by Bell (2004).

Solubility = 0.0178 + 0.0167 X Conc. of surfactant (% w/w) (5.14)

Table 5.12 gives the calculated solubility of cyanazine in different surfactants using the equation (5.14).

Table 5.12 Calculated solubility of cyanazine in different surfactants

Surfactant	Surf.rate g/l	Surfactant Conc %w/w	Cyanazine %w/w	Cyanazine Solubility in g/l
None	0	0	0.0178	0.178
C13E6	0.2	0.02	0.018134	0.18134
	1	0.1	0.01947	0.1947
	5	0.5	0.02615	0.2615
C13E11	0.2	0.02	0.018134	0.18134
	1	0.1	0.01947	0.1947
	5	0.5	0.02615	0.2615
C13E15	0.2	0.02	0.018134	0.18134
	1	0.1	0.01947	0.1947
	5	0.5	0.02615	0.2615
C13E20	0.2	0.02	0.018134	0.18134
	1	0.1	0.01947	0.1947
	5	0.5	0.02615	0.2615

Since the solubility of cyanazine is changing with concentration of surfactants therefore the initial droplet concentration of Cyanazine will also change. The new initial droplet concentrations of cyanazine are given in table 5.13.

Table 5.13 Initial droplet concentrations of cyanazine

Surfactant	Surf. rate (g/l)	Cyanazine Solubility (in g/l)	CdAl0 (mol/m3)	MAltotal (mol)	MAl0 (mol)
None	0	0.178	0.455243	4.17E-10	3.26E-10
C13E6	0.2	0.18134	0.45524	4.17E-10	3.26E-10
	1	0.1947	0.45529	4.17E-10	3.26E-10
	5	0.2615	0.45634	4.17E-10	3.25E-10
C13E11	0.2	0.18134	0.45524	4.17E-10	3.26E-10
	1	0.1947	0.45528	4.17E-10	3.26E-10
	5	0.2615	0.45627	4.17E-10	3.25E-10
C13E15	0.2	0.18134	0.45524	4.17E-10	3.26E-10
	1	0.1947	0.45528	4.17E-10	3.26E-10
	5	0.2615	0.45626	4.17E-10	3.25E-10
C13E20	0.2	0.18134	0.45524	4.17E-10	3.26E-10
	1	0.1947	0.45528	4.17E-10	3.26E-10
	5	0.2615	0.45625	4.17E-10	3.25E-10

Simulations were made with new diffusivity and solubility correlations for cyanazine and the results obtained are given below in table 5.14.

Table 5.14 Predicted % Uptake of Cyanazine at 24h and 120h

C yanazine + Surfactants	Surfactant Conc.(g/L)	24 hours		120 hours	
		Exp. % Uptake	Predicted % Uptake	Exp. %Uptake	Predicted % Uptake
None	0	6	1.14029	12	5.64442
C13E6	0.2	11	87.00181	16	99.29839
C13E6	1	28	99.08318	36	99.53515
C13E6	5	92	99.96009	96	99.90672
C13E11	0.2	10	9.61551	13	47.59655
C13E11	1	86	12.51118	87	61.93
C13E11	5	98	26.98949	99	99.33597
C13E15	0.2	21	4.92154	23	24.36149
C13E15	1	74	6.81088	78	33.71366
C13E15	5	98	16.25757	99	80.47454
C13E20	0.2	18	2.69781	19	13.35408
C13E20	1	50	3.76396	60	18.6315
C13E20	5	90	8.75218	98	43.32305

It can be seen that uptake for shorter chain ethoxy surfactant is very high whereas for longer chain the uptake is quite low so sensitivity analysis has to be performed on the diffusivity correlation analyzed above in order to look for most sensitive parameter which may be fitted in order to bring the model more close to real scenario. In is assumed that the major hindrance in uptake is given by the wax layer therefore more generalized equation were proposed for wax layer whereas no changes were made in diffusivity correlations for cuticle layer. More generalized correlations are given below;

$$\log D_{adj,wax} = K1 + K2 * C_{adj} - K3 * MV_{adj} \quad (5.15)$$

$$\log D_{adj,cutin} = -10.23 - 0.015 * MV_{adj} \quad (5.16)$$

$$\log D_{AI,wax} = K4 - K5 * MV_{AI} + K6 * C_{adj} \quad (5.17)$$

$$\log D_{AI,cutin} = -13 - 0.01 * MV_{AI} \quad (5.18)$$

Where;

D_{adj} and D_{AI} are diffusivity for surfactant and pesticide respectively in wax and cutin.

MV_{adj}, MV_{AI} are McGowan Volumes of surfactant and pesticide respectively.

C_{adj} is concentration of surfactant.

K1 –K6 are arbitrary parameters.

The sensitivity analysis was done in order to obtain the most sensitive parameter and can be seen from figure 5.3 below that K4 was highly sensitive.

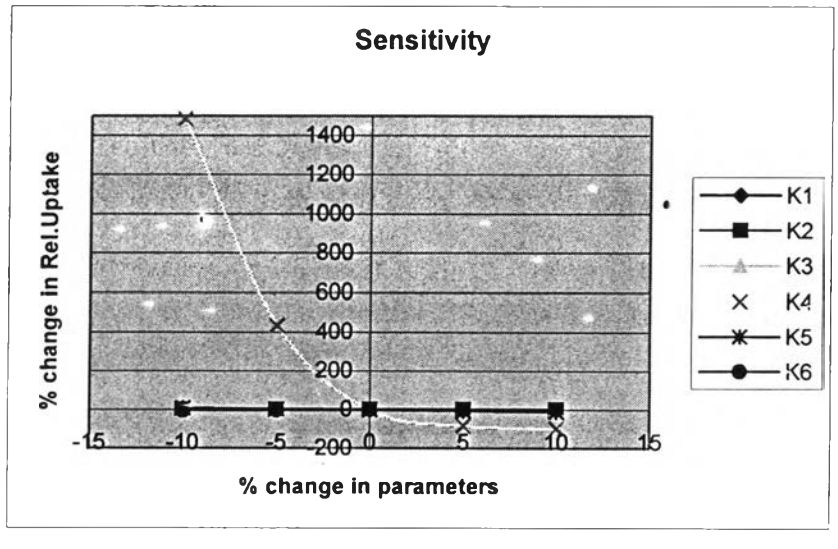

Figure 5.3 Sensitivity Analysis for new diffusivity correlation.

Keeping the other parameters constant, by trial and error it was found that the K4 values, which fit the experiment for Cyanazine with different surfactants, are given in table 5.15.

Table 5.15 Fitted values of K4 for Uptake of Cyanazine at 24h and 120h

Cyanazine + Surfactants	Surfactant Conc.(g/L)	24 hours			120 hours		
		Exp. Uptake %	Predicted Uptake%	K4	Exp. Uptake %	Predicted Uptake%	K4
None	0	6	6.35076	15.63	12	12.55044	16.1
C13E6	0.2	11	11.16502	17.38	16	16.31878	17.9
C13E6	1	28	28.41728	16.95	36	36.49995	17.54
C13E6	5	92	92.21973	16.415	96	96.52886	17.11
C13E11	0.2	10	10.13626	16.41	13	13.12875	17.01
C13E11	1	86	86.19175	15.288	87	87.14446	16.155
C13E11	5	98	98.07619	15.195	99	99.11977	16.095
C13E15	0.2	21	21.00859	15.72	23	23.00917	16.45
C13E15	1	74	74.07204	14.8	78	78.37315	15.87
C13E15	5	98	98.15832	14.57	99	99.12818	15.75
C13E20	0.2	18	18.14574	15.465	19	19.21414	16.26
C13E20	1	50	50.14177	14.52	60	60.329	15.71
C13E20	5	90	90.19397	14.01	98	98.30154	15.43

It was seen from table 5.14 that the diffusion of cyanazine with shorter chain ethoxylates was very high but for higher chain ethoxylates it decreased. So in order to fit the data K4 values were increased so as to slow down the diffusion of cyanazine with shorter chain ethoxylates whereas the values were lowered for higher chain ethoxylates in order to speed up the diffusion of cyanazine and this can be seen in table 5.15. Physically K4 is very important parameter as it represents the tortuosity factor, which is directly proportional to length of path pesticide needs to travel. So in order to bring the model more close to real scenario the path length was increased by increasing the K4 for formulation containing shorter chain surfactants and was decreased for formulation containing higher ethoxy chain length.

It was also assumed that the best-fit values of K4 could also be modeled as a function of surfactant properties, surfactant rate and time of uptake therefore following correlation for K4 was proposed.

$$K4(tu) = p1.e^{(-SR/0.34285)} + p3 + (p4.SR) - \left((120 - tu)0.00387 + Z.EO\right) \quad (5.19)$$

$$Z = 5.54001e-04 + \left(-4.58906e-04.e^{(-SR/0.66221)}\right) \quad (5.20)$$

$$p3 = 15.71455 + \left(14.39788.e^{(-EO/2.9549)}\right) \quad (5.21)$$

$$p4 = -0.54784 + \left(0.11428.EO\right) + \left(-0.00745.EO^2\right) + \left(1.47571E-4.EO^3\right) \quad (5.22)$$

Where;

SR is surfactant rate in g/l

EO is the number of ethoxy unit in surfactant

tu is the uptake time in hours.

Figure 5.4 shows the comparison of experimental results with the predicted ones by using the above uptake model, before and after fitting of one model-parameter.

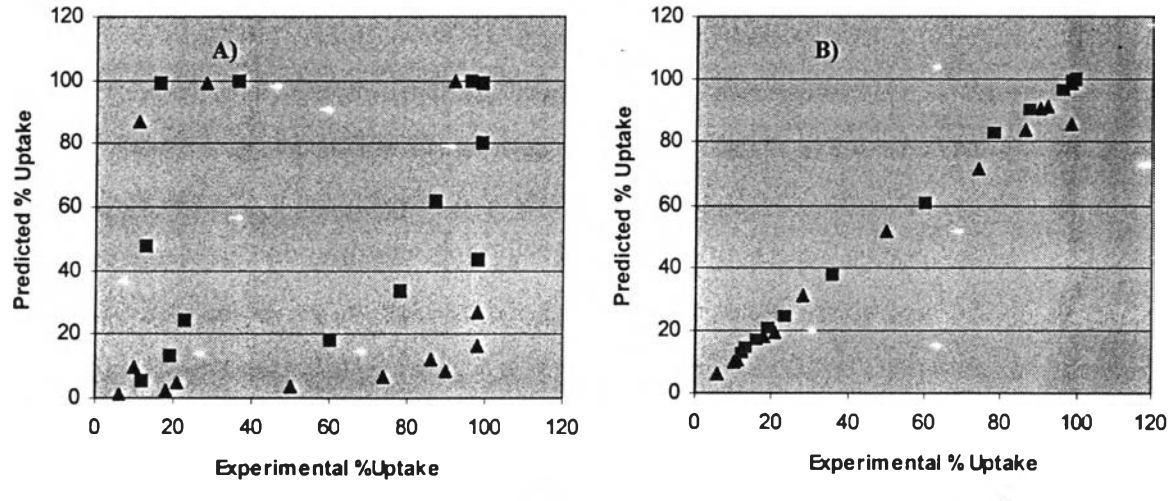

Figure 5.4 Predicted Uptake vs. Experimental Uptake for Cyanazine at 24h(▲) and 120h(■):A) Before Parameter fitting, B) After Parameter Fitting.

5.3 Pesticide Formulation Design: Case Studies

The use of the pesticide formulation framework as described in figure 2.1 is illustrated here with a Design problem.

Problem Definition: To design an efficient Pesticide formulated to be used on wheat plant

Step1. It is desirable to make a formulation of pesticide and surfactant for wheat plant, therefore, in the first step the wheat plant will be selected and the data related to thickness of wax, cuticle in leaf and volume of plant (plant corresponds to all parts below the epidermis of leaf) corresponding to wheat plant will automatically be taken from the database and model preparation tool.

Step2. In the next step pesticide (active ingredient) needs to be chosen, several pesticides with their properties are available in database to chose from (for example Cyanazine and Phenyl urea), Since user needs to formulate for Cyanazine and Phenyl urea so they will be selected one by one and there corresponding properties and their related property model parameters will be retrieved from the database. The database will give pure component properties whereas the property estimation tools will provide necessary solubility and diffusivity data. The initial concentration of pesticide will be fixed at 0.5g/l

Step3. The framework will next assist in selecting different candidate surfactants, four different linear alkane ethoxylates having different ethoxy chain length where chosen to be combined with each pesticide. Each surfactant will be used in three different concentration of 0.2,1 and 5 g/l This will give twelve different formulations for each pesticide and each of them will be tested using the uptake model.

Step4. The Uptake behavior of pesticide formulation was predicted at different times with the help of pesticide uptake model.

5.3.1 Case study 1: Cyanazine

First the simulations were performed for formulations containing Cyanazine.The uptake was predicted at 24h and 120h respectively. The results obtained are validated with the experimental results (see figure 5.4) and are shown in table 5.16.

Table 5.16 Percentage Uptake of Cyanazine at 24h and 120h

Cyanazine + Surfactants		24 Hours				120 hours			
	Surfactant Conc.(g/L)	Exp. Uptake %	95 % upper conf lim	95% lower conf lim	Predicted Uptake %	Exp. Uptake %	95 % upper conf lim	95% lower conf lim	Predicted Upake %
None	0	6	13.1	-1.1	6.35076	12	17.9	6.1	12.6
C13E6	0.2	11	18.1	3.9	10.59045	16	21.9	10.1	16.9
C13E6	1	28	35.1	20.9	31.18483	36	41.9	30.1	37.3
C13E6	5	92	99.1	84.9	91.32031	96	101.9	90.1	96.1
C13E11	0.2	10	17.1	2.9	10.09805	13	18.9	7.1	14.6
C13E11	1	86	93.1	78.9	84.05387	87	92.9	81.1	90.2
C13E11	5	98	105.1	90.9	99.07619	99	104.9	93.1	99.4
C13E15	0.2	21	28.1	13.9	19.13981	23	28.9	17.1	24.6
C13E15	1	74	81.1	66.9	71.27519	78	83.9	72.1	82.8
C13E15	5	98	105.1	90.9	86.00733	99	104.9	93.1	99.9
C13E20	0.2	18	25.1	10.9	17.81544	19	24.9	13.1	20.4
C13E20	1	50	57.1	42.9	51.36825	60	65.9	54.1	60.3
C13E20	5	90	97.1	82.9	90.99397	98	103.9	92.1	99.4

It can be seen in figure 5.5 that the addition of surfactant has increased the uptake by almost one order of magnitude as compared to the formulation in which there was no surfactant.

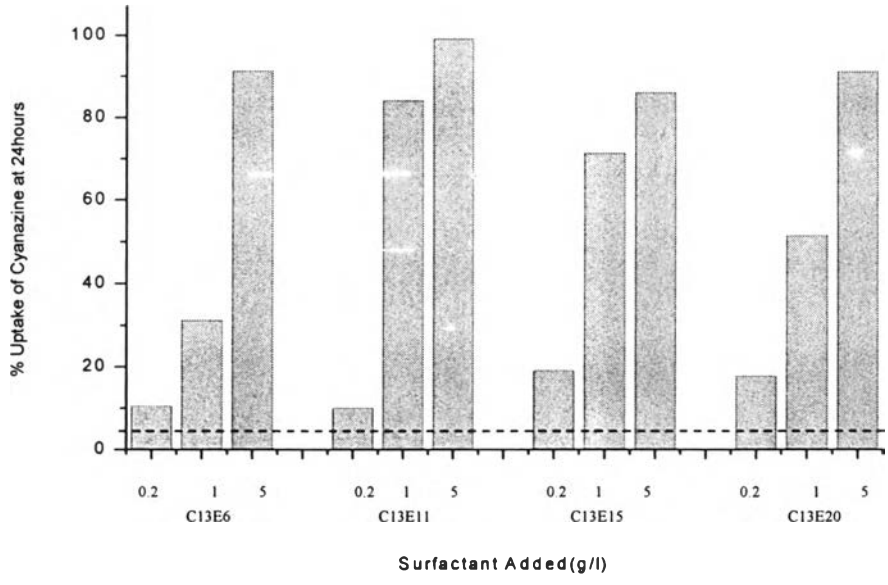

Figure 5.5 Effects of ethylene oxide content and concentration of aliphatic alcohol surfactants on uptake of Cyanazine at 24hours after application to wheat plant. Dotted lines indicates uptake of the compound in absence of surfactants.

The uptake has also increased with the concentration of surfactant as well as with the time as shown in figure 5.6.

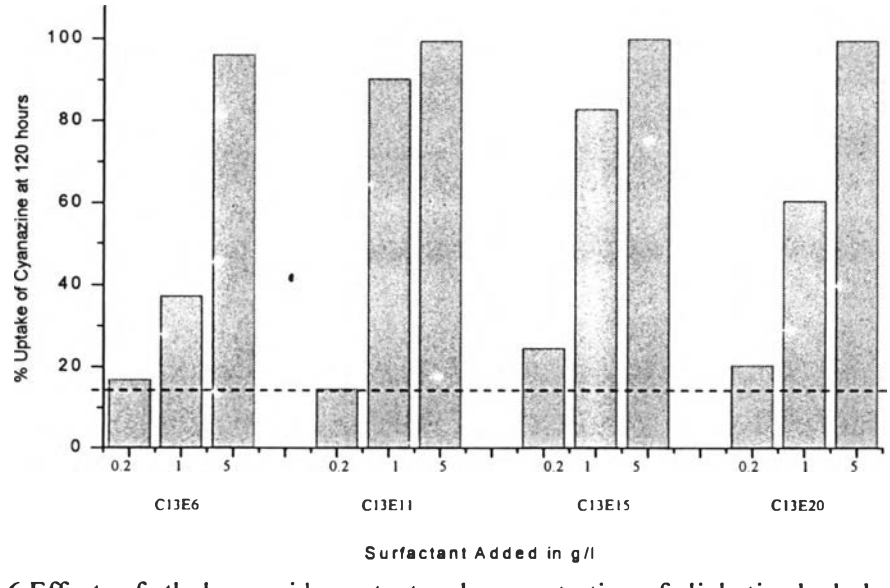

Figure 5.6 Effects of ethylene oxide content and concentration of aliphatic alcohol surfactants on uptake of Cyanazine at 120hours after application to wheat plant. Dotted lines indicates uptake of the compound in absence of surfactants.

At lower concentration the surfactant with long ethoxy unit has more significant effect on uptake as compared to surfactant with shorter ethoxy unit. If one has to use formulation with a surfactant concentration of 0.2g/l than surfactant with fifteen-ethoxy unit is highly desirable whereas if surfactant concentration of 5g/l is put in formulation than surfactant with eleven-ethoxy unit is recommended to be used in formulation.

The uptake model also gives the variation of relative uptake of active ingredient and adjuvant with time. Graphical result for the experiment containing cyanazine as the pesticide with C13E11 as surfactant with concentration of 0.2g/l and 1g/l are shown in figure 5.7 and 5.8 respectively.

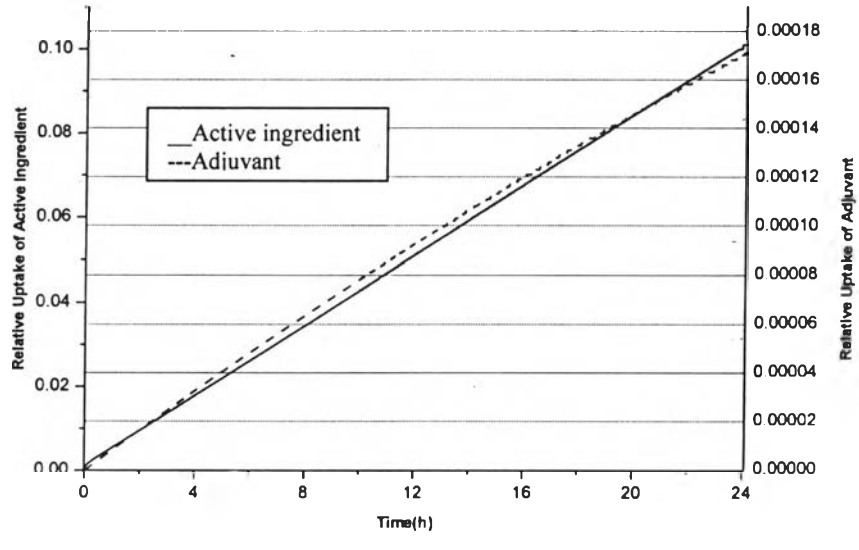

Figure 5.7 Relative uptake of AI (Cyanazine) and adjuvant (C13E11) at 24 hours with surfactant concentration of 0.2 g/l.

It can be seen that the relative uptake of adjuvant is very small as compared to the relative uptake of active ingredient. On increasing the concentration of adjuvant from 0.2 g/l to 1g/l (see figure 5.8) its uptake has not increased significantly but it has helped the active ingredient to diffuse faster and hence we can see a significant increase in uptake of active ingredient.

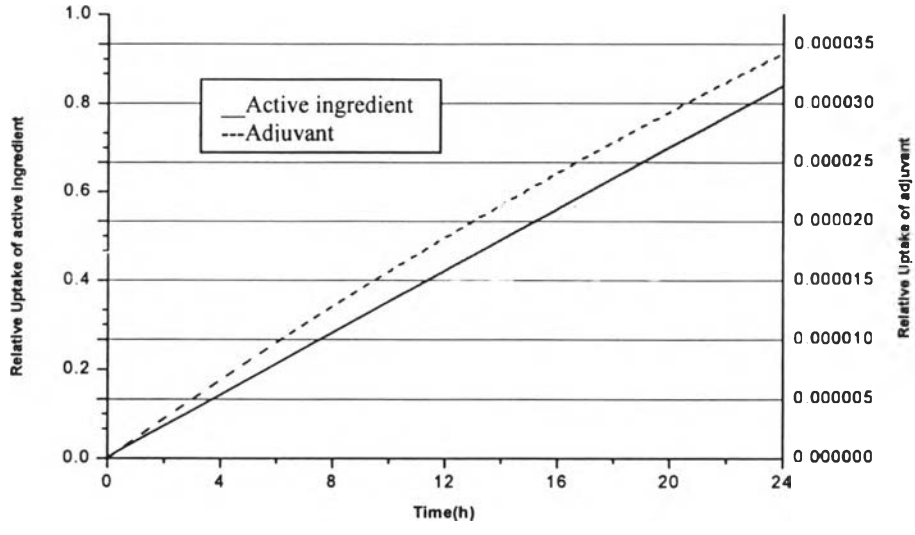

Figure 5.8 Relative uptake of AI (Cyanazine) and adjuvant (C13E11) at 24 hours with surfactant concentration of 1 g/l.

This is because an increase in adjuvant concentration in droplet has increased the solubility of active ingredient in the droplet therefore driving force for diffusion of active ingredient has also increased which results in higher uptake.

5.3.2 Case Study 2: Phenyl Urea

Next the simulations are performed using Phenyl urea. The corresponding pesticide properties and its related property model parameters are retrieved from the database. Similar algorithm, as described from step 1 to step 4 was followed.

The Uptake behavior of Phenyl urea formulation was predicted at 8 hours and 24 hours using the uptake model and results are shown in table 5.17.

Table 5.17 Percentage Uptake of Phenyl urea at 8h & 24h

Phenyl Urea + Surfactants	Surfactant Conc.(g/L)	8 hours % Uptake Phenyl Urea	8 hours %Uptake Surfactants	24 hours % Uptake Phenyl Urea	24 hours %Uptake Surfactants
None	0	0.29901	0	0.8904	0
C13E6	0.2	0.72323	1.98272	1.79217	3.63289
C13E6	1	3.28626	0.39654	9.41671	0.72658
C13E6	5	9.87053	0.07913	29.13161	0.14498
C13E11	0.2	1.07215	0.00639	3.1658	0.01709
C13E11	1	13.1805	0.00128	39.46658	0.00342
C13E11	5	15.78485	2.56E-04	47.27063	6.85E-04
C13E15	0.2	2.6876	2.22E-05	8.03482	6.63E-05
C13E15	1	15.63316	4.42E-06	46.81693	1.32E-05
C13E15	5	29.27257	8.88E-07	87.60641	2.66E-06
C13E20	0.2	2.54415	8.41E-09	7.61485	2.52E-08
C13E20	1	12.89309	3.09E-09	38.59948	9.28E-09
C13E20	5	24.7948	6.18E-10	74.14188	1.85E-09

It can be seen that uptake of Phenyl urea has increased with the concentration of surfactant used in the formulation as well as with time. Type of surfactant used in formulation also effects the uptake behaviour. An increase in ethoxy unit in the surfactant has increased the uptake of phenyl urea (see figure 5.9). These again suggest that the surfactant plays a role more than just improving spreading. The most optimum surfactant to be used in formulation is C13E15, which has significant effect on uptake of phenyl urea both at lower and higher surfactant concentrations.

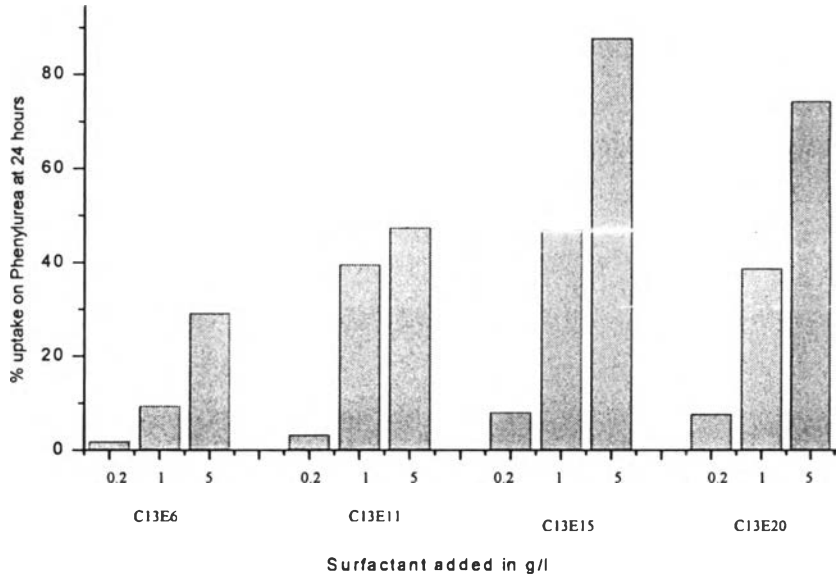

Figure 5.9 Effects of ethylene oxide content and concentration of aliphatic alcohol surfactants on uptake of Phenyl urea at 24hours after application to wheat plant.

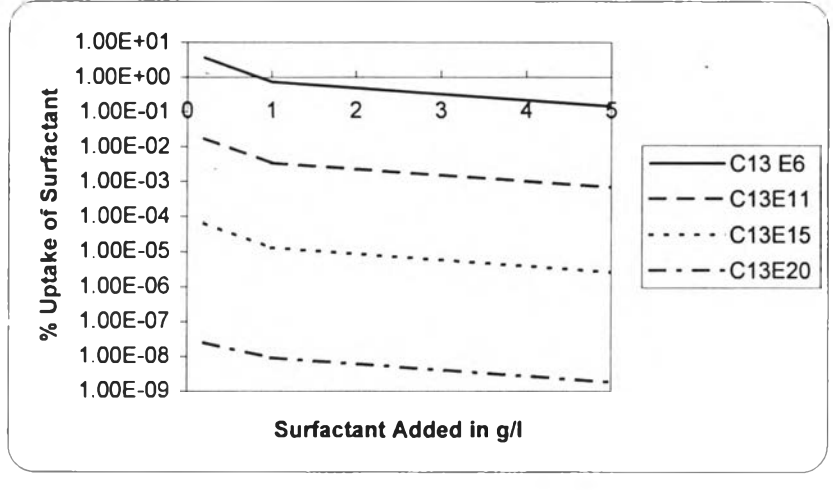

Figure 5.10 Percentage Uptake of surfactants.

Figure 5.10 shows the uptake of surfactants with change in its concentrations. It can be seen that uptake of lower ethoxy unit surfactant (C13E6) is higher as compared to surfactants with longer chain ethoxy unit (C13E20). This may be due to the lengthy structure of surfactant, which makes it difficult to pass through the wax and cuticle layers of the leaf. Although it was seen that higher the ethoxy unit and concentration of surfactant in formulation higher is the uptake of pesticide. Therefore it again verifies that surfactant is not only increasing the spreading of droplet but also

enhancing the diffusion of pesticide. The exact physical mechanism of surfactant inside the leaf wax is difficult to find.

In this way we can see that with the help of framework several product alternatives where obtained and evaluated so that the appropriate design decision can be made based on the uptake behavior of the pesticide. Incase the user needs to design formulation using Cyanazine than surfactants with fifteen ethoxy unit was most desirable for lower concentration of surfactant in formulation but if high concentration of surfactant is put in formulation than surfactant with eleven ethoxy unit was most optimum to be used in formulation, Similarly if instead of using cyanazine in formulation the user wish to have phenyl urea in his formulation than it can be seen that surfactant with fifteen ethoxy unit was more effective. In this way several alternatives were generated and was made available for user to make decision.

The main advantage of this framework is related to the systematic step-by-step solution approach, the efficient data storage/transfer and the predictive capabilities of the models, resulting in the simplification of the analysis of the formulation alternatives and the evaluation of their performance.