Mathematical Modelling for Dielectric Studies of Molecular Interactions of Anilines with2-butoxy Ethanol

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ABSTRACT

The moment of dipole of the 1:1 complexes of 2-butoxy ethanol with aniline, o-chloro aniline, p-chloro aniline at 303K have been identified by using Huysken's method. The increments of dipolar were computed using bond angle in the molecular orbital theory. The improvement of the dipole moment values assures the hydrogen bonding between the systems. RSM is the techniques that are to model and analyze the problems that involves several variables for optimizing this response. The measured and the predicted values are near to the established equations clearly show that all the parameters influence the complex formation. So the response equations for the molecular interactions and the complex formation evolved through past data Design can be successfully predict the complex formation of any combination of the experimental results.

KEY WORDS: 2-butoxy ethanol, H-Bonding, Dipole moment, Aniline.

1. INTRODUCTION

The moment of dipole μ_{AB} of the complex produced between acceptor group B and the proton donor group A-H. The inert solvent solutes of Dielectric investigation give data about solutions of molecular complexes and structure (Balamuralikrishnan, 2006). The large dipole moment and constant of dielectric is formed because of A-H (Proton donor) polarity increment due to hydrogen bond formation. Complexes of hydrogen bonded stereo chemistries has been determined from the inert solvent proton acceptor. Charge – transfer interaction, electrostatic and polarization creates electron density distribution of bonded complexes of hydrogen that indicates the interactions of complexes formation (Huyskens, 1990). The bond moment $\Delta\mu$ enhances OH distance increase due to hydrogen bond. The sum of charges along the A-H…..B Bond is lesser than complexes of dipole moment. The aniline – ethanol complex formation using Onsager's method is discussed in this paper (Onsagar, 1936).

2. EXPERIMENTAL

Dipole meter RL09 Toshniwal with 300 kHz static frequency is used for dielectric measurements and it is calibrated using liquids. Water is circulated through cell's glass jacket to maintain the cell temperature at 303K. The Refractive indices at cell temperature of 303K are measured by Abbe's refractometer. The density is measured by Specific gravity bottle and chemicals purification is done using standard procedure and these values are checked against literature values.

Theory: Solute-solvent based mixtures of all dipole moment was obtained using Huyskens methods. This is best for ternary mixtures that contains B (acceptor) in an apolar solvent and two polar components A (donor) (Huyskens, 1990). Using the Onsager theory (Onsagar, 1936) the dipole moment [M]of a solution of polar substances and a polar solvent is given by:

Considering the ternary mixture of polar components A (-OH group) and B (-NH_2 group) in a non- polar solvent, the relative orientations of A and B vary continuously because of the mobility of the liquid phase. The dipole moment solution may be written as $M^2 = \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} N_{ij}\mu_{ij}$ (1)

Where N is the number of ij ensembles. Huyskens (1990) showed that equation.1 can be written as

$$M^2 = \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} N_{ij} \left[\frac{\mu_{ij}^2 - j<\mu_{oj}/j>}{i}\right] + n_B < \mu_{oj}^2 / j > N_B \quad (2)$$

Where $<\mu_{oj}/j>$ is the mean square of the B, j is taken as 1 and $<\mu_{oj}/j>$ is practically μ_b^2.

The quantity $\frac{\mu_{ij}^2 - \mu_{oj}/j>}{i}$ represents the mean share of the A molecule.

$$n_A = \sum_{i=0}^{\infty} iN_{ij}/N_A \quad (3)$$

$$n_B = \sum_{i=0}^{\infty} iN_{ij}/N_B \quad (4)$$

$$\frac{M^2}{VN_A} = \left(< \mu_{ab}^2 - \mu_b^2 > C_a + < \mu_b^2 > C_b\right) \quad (5)$$

Where $C_a$and C_b are the formal concentration (mol dm^{-3}).

$$M^2 = \frac{9KT}{4\pi}\left[\frac{(\epsilon_0 - n_D^2)(2\epsilon_0 + n_D^2)}{\varepsilon_0 (n_D^2+2)^2}\right] - \frac{F_s}{\bar{F}_s}\left[\frac{(\epsilon_s - n_{DS}^2)(2\epsilon_S + n_{DS}^2)}{\varepsilon_S (n_{DS}^2+2)^2}\right] \quad (6)$$

Is the actual concentration of the polar solvent and $\bar{F}_s$ is the concentration in its pure state. Substitute equation

$$(< \mu_{ab}^2 - \mu_b^2 >)\frac{c_a}{c_b} + \mu_b^2\Omega_B = \left[\frac{(\epsilon_0 - n_D^2)(2\epsilon_0 + n_D^2)}{\varepsilon_0 (n_D^2+2)^2}\right] - \frac{F_s}{F_s}\left[\frac{(\epsilon_s - n_{DS}^2)(2\epsilon_s + n_{DS}^2)}{\varepsilon_s (n_{DS}^2+2)^2}\right] \quad (7)$$

If μ_a, μ_b and μ_{ab} are the dipole moments that consists of proton donor, proton acceptor and their 1:1 complexes. Huyskens (1990), showed that: $M^2 = V N_A (\bar{\mu}_{ab}^2 - \bar{\mu}_b^2) C_A + \bar{\mu}_b^2 C_B$ (8)

The experimental values for various concentrations for the system are given in Table.1.

Table.1. Values of Dielectric Constant, Refractive Index and Density of aniline, o-chloro aniline and p-chloro aniline with the formal concentration of 2- butoxyethanol 2-butoxyethanol +aniline in cccl$_4$ System

Mole Fraction of the Solute X_2	Dielectric Constant of the Solution ε_{12}	Refractive Index of the Solution n_{12}	Density of the Solution d_{12}	Ω_B	μ_b^2
0.05	1.4523	1.3938	1.6414	86.250	86.265
0.1	1.516	1.3934	1.6356	73.522	73.537
0.2	1.7076	1.3930	1.6256	6.3009	6.3009
0.3	1.9001	1.3926	1.6164	14.1287	14.1287
0.4	2.054	1.3822	1.6099	8.7835	8.735
0.5	2.407	1.3818	1.6005	5.7732	5.7886

2-butoxyethanol + o-chloro aniline in ccl$_4$ System

Mole Fraction of the Solute X_2	Dielectric Constant of the Solution ε_{12}	Refractive Index of the Solution n_{12}	Density of the Solution d_{12}	Ω_B	μ_b^2
0.05	2.1808	1.3739	1.6336	45.526	45.806
0.1	2.1914	1.3737	1.6293	20.050	20.069
0.2	2.2892	1.3724	1.6288	10.154	10.173
0.3	2.3387	1.3721	1.6214	6.1395	6.1587
0.4	2.3858	1.3715	1.5988	8.4579	8.477
0.5	2.4372	1.3710	1.5962	3.2321	3.055

2-butoxyethanol + p-chloro aniline in ccl$_4$ System

Mole Fraction of the Solute X_2	Dielectric Constant of the Solution ε_{12}	Refractive Index of the Solution n_{12}	Density of the Solution d_{12}	Ω_B	μ_b^2
0.05	2.1623	1.3730	1.6380	43.1827	43.2039
0.1	2.191	1.3728	1.6369	20.204	20.225
0.2	2.3190	1.3725	1.6367	10.850	10.871
0.3	2.3209	1.3721	1.6318	5.9098	5.9313
0.4	2.3877	1.3712	1.6314	4.2856	4.307
0.5	2.4867	1.3701	1.6296	3.519	3.540

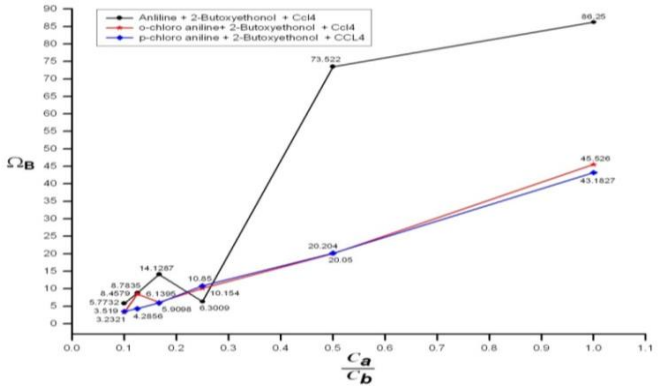

Figure.1. The formation of a 1: 1 complex aniline, o-chloro aniline and p-chloro aniline with the formal concentration (C_a/C_b) of 2- butoxyethanol with Ω_B

Table.2. Dipole Moments of the Components and their 1: 1 Complexes and Dipolar Increments of the Complexes

2-butoxyethanol+ anilines

Systems	μ_a(D)	μ_b(D)	μ_{ab}(D)	$\Delta\mu$(D)
2-Butoxyethanol + Aniline+ CCl_4	1.5	1.73	7.33	7.55
2-Butoxyethanol + o-chloro aniline + CCl_4	1.8	2	6.46	6.74
2-Butoxyethanol + p-chloro aniline + CCl_4	3.1	1.22	7.07	7.35

3. RESULTS AND DISCUSSION

A dipole moment of proton donor μ_a forms a H-bond with a dipole moment of proton acceptor μ_b. At this time, calculation of dipolar increment is done. If the values θ_a and θ_b differs from zero. The plot of (C_a/C_b) with Ω_B is straight line which indicate the possibility of a 1: 1 complex formation (Fig 2). The plot of (C_a/ C_b) with Ω_B is straight line which shows the possibility of a 1:1 complex formation. The values are small, sometimes even negative. This explains the nonexistence of effects of charge transfer. If charge transfer effect is present, $\Delta\mu$ would be greater (Bauge, 1964) than 10D. As $\Delta\mu$ is less than 10 D, it may be inferred that the complexion may be only due to redistribution of electrons due to polarization effects. The dipole moments for the system 2-butoxy ethanol in aniline > p-chloro aniline > o-chloro aniline in the order of 7.55D >7.35 D > 6.74D >

Therefore it is inferred that the system's dipolar increment is small because of the Polarization effect and charge transfer phenomenon.

Response surface methodology, the historical data design and the Response equation: The Historical data design is a self-governing quadratic design that does not have an embedded factorial.

Anova: ANOVA is used to calculate the molecular interaction of the ternary liquid system Design Expert 7.0 is used to show the validation of the observed values and the results were discussed below in tables 3-5. Tables 3-5 give the model statistics. It show that linear model is the best-suggested model. It also gives the ANOVA results for the Response Surface Linear Model of the input parameters. Table.6 presents the Regression Statistics.

Table.3. Results of ANOVA for Response Surface Linear Model

(2-butoxyethanol +aniline in ccl_4 System)

Response 1(Dielectric Constant)					
Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob> F**
Model	0.63	1	0.63	189.76	0.0002
B-Y2	0.63	1	0.63	189.76	0.0002
Residual	0.013	4	3.32E-03		
Cor Total	0.64	5			
Response 2(Refractive Index)					
Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob> F**
Model	0.000132	1	0.000132	14.69856	0.0186
B-Y2	0.000132	1	0.000132	14.69856	0.0186
Residual	3.6E-05	4	8.99E-06		
Cor Total	0.000168	5			
Response 3(Density)					
Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob> F**
Model	0.001207	1	0.001207	776.0521	< 0.0001
B-Y2	0.001207	1	0.001207	776.0521	< 0.0001
Residual	6.22E-06	4	1.56E-06		
Cor Total	0.001213	5			
Response 1 (Dielectric Constant)					
Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob> F**
Model	0.053	1	0.053	223.07	0.0001
B-Y2	0.053	1	0.053	223.07	0.0001
Residual	9.46E-04	4	2.37E-04		
Cor Total	0.054	5			
Response 2 (Refractive Index)					
Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob> F**

Model	6.53E-06	1	6.53E-06	99.81271	0.0006
B-Y2	6.53E-06	1	6.53E-06	99.81271	0.0006
Residual	2.62E-07	4	6.54E-08		
Cor Total	6.79E-06	5			
Response 3(Density)					
Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob> F**
Model	0.001201	1	0.001201	33.84538	0.0043
B-Y2	0.001201	1	0.001201	33.84538	0.0043
Residual	0.000142	4	3.55E-05		
Cor Total	0.001343	5			
Response 1(Dielectric Constant)					
Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob> F**
Model	0.070099	1	0.070099	84.26536	0.0008
B-Y2	0.070099	1	0.070099	84.26536	0.0008
Residual	3.33E-03	4	8.32E-04		
Cor Total	0.073427	5			
Response 2(Refractive Index)					
Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob> F**
Model	5.72E-06	1	5.72E-06	54.8	0.0018
B-Y2	5.72E-06	1	5.72E-06	54.8	0.0018
Residual	4.17E-07	4	1.04E-07		
Cor Total	6.14E-06	5			
Response 3(Density)					
Source	Sum of Squares	df	Mean Square	F Value	p-value Prob> F
Model	5.81E-05	1	5.81E-05	51.64155	0.0020
B-Y2	5.81E-05	1	5.81E-05	51.64155	0.0020
Residual	4.5E-06	4	1.13E-06		
Cor Total	6.26E-05	5			

Table.6. Regression Statistics

Statistical Values	**2-butoxyethanol +aniline in ccl_4 System**			**2-butoxyethanol + o-chloro aniline in ccl_4 System**		
	ε_{12}	n_{12}	d_{12}	ε_{12}	n_{12}	d_{12}
Std. Dev.	0.041	3.00E-03	1.25E-03	0.015	2.56E-04	5.96E-03
Mean	1.84	1.39	1.62	2.3	1.37	1.62
C.V. %	2.25	0.22	0.077	0.67	0.019	0.37
PRESS	0.042	6.61E-05	1.35E-05	1.98E-03	5.32E-07	2.58E-04
R-Squared	0.992	0.7861	0.9949	0.9824	0.9615	0.8943
Adj R-Squared	0.9867	0.7326	0.9936	0.978	0.9518	0.8679
Pred R-Squared	0.9343	0.6067	0.9889	0.9632	0.9217	0.808
Adeq Precision	31.537	7.662	55.677	29.851	19.968	11.627

Statistical Values	**2-butoxyethanol + p-chloro aniline in ccl_4 System**		
	ε_{12}	n_{12}	d_{12}
Std. Dev.	0.029	3.23E-04	1.06E-03
Mean	2.31	1.37	1.63
C.V. %	1.25	0.024	0.065
PRESS	5.91E-03	1.21E-06	7.08E-06
R-Squared	0.9547	0.932	0.9281
Adj R-Squared	0.9434	0.915	0.9101
Pred R-Squared	0.9195	0.8036	0.887
Adeq Precision	18.347	14.795	14.363

The Value of " Probability > F" & less than 0.05 shows that the model terms are significant, which is enviable as indicated that the response of the model has significant effect. This model is used to find the way to the design space. Table.6 gives the regression statistics. The coefficient of determination R^2 is used to decide whether a regression model is appropriate or not. In this study, the coefficient of determination R^2 an exact match if it is 1 and if the residual increases R^2 decreases in the range from 1 to 0. Also it is observed that the "Pred R-Squared" is in good conformity with the "Adj R-Squared" in all the output parameters. Moreover "Adeq Precision" shows the signal to noise ratio. A ratio of greater than 4 is wanted. In this study, the ratio obtained shows an adequate signal in all the parameters. The effectiveness of the model has been checked by the validation with experimental values. The experimental results are validated by asserting that the predicted values are very close to each other and hence the developed models are suitable.

4. CONCLUSIONS

- The experimental data compared with RSM model is be effectively related the above process parameters with the molecular interactions and the complex formation.
- The established equations clearly show that all the parameters influence the complex formation. The predicted and the measured values are very close to each other which indicate that the developed model is to be used for predicting the complex formation along with the experimental results having more than 95% confidence level.

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