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STATISTICAL ANALYSIS OF EXPERIMENTAL RESULTS FOR DIELECTRIC STUDIES IN MOLECULAR INTERACTIONS OF ANILINES WITH 2-METHOXYETHANOL IN CCL_4 SYSTEM BY RSM MODEL

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Abstract

The moment of dipole of the 1:1 complexes of 2-methoxyethanol 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 analyse 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.

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

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dielectric investigation give data about solutions of molecular complexes and structure (Balamuralikrishnan, [1]). 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 have 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, [4]). The bond moment $\Delta\mu$ enhances OH distance increase due to hydrogen bond. The sum of charges along the $A-H\ldots B.$ Bond is lesser than complexes of dipole moment. The aniline-ethanol complex formation using Onsager's method and the results of the experimental data are analysed by statistical method is discussed in this paper (Onsagar, [8]).

Experimental

Dipole meter RL09 Toshniwal with 300kHz 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.

Table I. Values of dielectric constant, refractive index and density of aniline with the formal concentration of 2-methoxyethanol in CCL_4 system.

Mole Fraction of the Solute (mol/L)	Dielectric Constant of the Solution ε_{12}	Refractive Index of the Solution n_{12}	Density of the Solution d_{12} (Kg/m3)	$\Omega_B \times 10^{39}$	μb^2
0.05	2.0453	1.489	1.6390	17.4628	17.477
0.1	2.1041	1.4791	1.6379	5.0332	5.048
0.2	2.1103	1.4770	1.6377	1.6405	1.655

0.3	2.223	1.4750	1.6372	0.5724	0.5874
0.4	2.2404	1.4730	1.6368	0.5192	0.5337
0.5	2.260	1.4710	1.6319	0.5195	0.5195

Table-II. Values of dielectric constant, refractive index and density of o-chloroaniline with the formal concentration of 2-methoxyethanol in CCL_4 system.

Mole Fraction of the Solute (mol/L)	Dielectric Constant of the Solution ε_{12}	Refractive Index of the Solution n_{12}	Density of the Solution d_{12} (Kg/m3)	$\Omega_B \times 10^{39}$	μb^2
0.05	2.0472	1.4044	1.6408	11.518	11.518
0.1	2.1816	1.4042	1.6350	11.133	11.1452
0.2	2.2209	1.3940	1.6339	6.8657	6.8778
0.3	2.2397	1.3938	1.6329	3.9643	3.9764
0.4	2.3582	1.3936	1.6323	3.4717	3.4839
0.5	2.3780	1.3932	1.6303	2.4969	2.5096

Table-III. Values of dielectric constant, refractive index and density of p-chloroaniline with the formal concentration of 2-methoxyethanol in CCL_4 system.

Mole Fraction of the Solute (mol/L)	Dielectric Constant of the Solution ε_{12}	Refractive Index of the Solution n_{12}	Density of the Solution d_{12} (Kg/m3)	$\Omega_B \times 10^{39}$	μb^2
0.05	2.1163	1.4041	1.6408	22 .0359	22.0496
0.1	2.2317	1.3938	1.6350	18.572	18.5858
0.2	2.2602	1.3936	1.6329	7.8267	7.8403

0.3	2.3170	1.3932	1.6323	4.97234	4.9859
0.4	2.3877	1.3828	1.6329	3.9758	3.9894
0.5	2.4165	1.3823	1.6249	2.9092	2.9228

Table IV. Dipole moments of the components and their 1:1 complexes and dipolar increments of the complexes 2-methoxyethanol + anilines.

Systems	$\mu_a(D)$	$\mu_b(D)$	$\mu_{ab}(D)$	$\mu(D)$
2-Methoxyethanol + Aniline+ CCl_4	1.5	0.707	4.5	4.1
2-Methoxyethanol + o-Chloroaniline + CCl_4	1.8	1.4	3.9	3.6
2-Methoxyethanol + p-Chloroaniline + CCl_4	3.1	1.1	5.5	4.7

Results and Discussion

A dipole moment of proton donor μ_a forms an 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 differ from zero. The plot of (Ca/Cb) with Ω_B is straight line which indicate the possibility of a 1:1 complex formation (Figure 1). μ_a, μ_b and μ_{ab} are the dipole moments that consists of proton donor, proton acceptor and their 1:1 complexes. Huyskens [4] showed that $M^2 = V N_A(\mu^{\overline{2}}ab - \mu^{\overline{2}}b)C_A + \mu^{\overline{2}}bC_B$. The experimental values for various concentrations for the system are given in Table 4. The plot of (Ca/Cb) 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, [2]) than 10D. As $\Delta\mu$ is less than 10D, 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-methoxy ethanol in p-chloro aniline > aniline > o-chloro aniline in the order of 4.7 D > 4.1 D > 3.6 D. 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 an independent quadratic design, that does not contain an embedded factorial or factorial design (Cochran, Montogomery, [3], [7]). In [3, 7] the experimental values are analysed to determine the molecular interaction of the ternary liquid system, the Analysis of Variance (ANOVA) was employed to identify the level of importance in interaction parameters on their performance characteristics. The effect of these parameters on interaction has been investigated using experimental designs and the variation of this interaction parameter with the dipole increment was discussed in terms of molecular interaction. A new software verification technique called Design Expert 7.0 was used to reveal the validity of the observed values developed and the results were discussed below in tables 5-7. Tables 5-7 give the model statistics. It reveals that linear model is the best-suggested model. So, for further analysis this model was used. It also provides the ANOVA results for the response surface linear model of the input parameters and is commonly used to summarize the test for significance on individual model coefficients. Table 8 presents the regression statistics.

Table V. Results of ANOVA for response surface linear model (2-methoxyethanol + aniline in CCL_4 system).

Response 1 (Dielectric Constant)					
Source	Sum of Squares	df	Mean Square	F Value	p-value Prob> F
Model	0.036	1	0.036	44.02	0.0027
B-Y2	0.036	1	0.036	44.02	0.0027
Residual	3.256E-003	4	8.141E-004		
Cor Total	0.039	5			
Response 2 (Refractive Index)					

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob> F
Model	1.600E-004	1	1.600E-004	14.64	0.020
B-Y2	1.600E-004	1	1.600E-004	14.64	0.020
Residual	4.370E-005	4	1.092E-005		
Cor Total	2.037E-004	5			
Response 3 (Density)					
Source	Sum of Squares	df	Mean Square	F Value	p-value Prob> F
Model	2.256E-005	1	2.256E-005	10.68	0.0308
B-Y2	2.256E-005	1	2.256E-005	10.68	0.0308
Residual	8.450E-006	4	2.113E-006		
Cor Total	3.102E-005	5			

Table VI. Results of ANOVA for response surface linear model (2-Methoxyethanol + O -Chloroaniline in CCL_4 System).

Response 1 (Dielectric Constant)					
Source	Sum of Squares	df	Mean Square	F Value	p-value Prob> F
Model	0.067	1	0.067	36.12	0.0039
B-Y2	0.067	1	0.067	36.12	0.0039
Residual	7.370E-003	4	1.842E-003		
Cor Total	0.074	5			
Response 2 (Refractive Index)					

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob> F
Model	1.073E-004	1	1.073E-004	9.69	0.0357
B-Y2	1.073E-004	1	1.073E-004	9.69	0.0357
Residual	4.428E-005	4	1.107E-005		
Cor Total	1.516E-004	5			
Response 3 (Density)					
Source	Sum of Squares	df	Mean Square	F Value	p-value Prob> F
Model	4.973E-005	1	4.973E-005	13.20	0.0221
B-Y2	4.973E-005	1	4.973E-005	13.20	0.0221
Residual	1.507E-005	4	3.768E-006		
Cor Total	6.480E-005	5			

Table VII. Results of ANOVA for response surface linear model (2-Methoxyethanol + P - Chloroaniline in CCL_4 System).

Response 1 (Dielectric Constant)					
Source	Sum of Squares	df	Mean Square	F Value	p-value Prob> F
Model	0.056	1	0.056	53.54	0.0019
B-Y2	0.056	1	0.056	53.54	0.0019
Residual	4.22E-003	4	1.055E-003	-	-
Cor Total	0.061	5	-	-	-
Response 2 (Refractive Index)					

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob> F
Model	2.775E-004	1	2.775E-004	20.54	0.0106
B-Y2	2.775E-004	1	2.775E-004	20.54	0.0106
Residual	5.405E-005	4	1.351E-005	-	-
Cor Total	3.316E-004	5	-	-	-
Response 3 (Density)					
Source	Sum of Squares	df	Mean Square	F Value	p-value Prob> F
Model	1.019E-004	1	1.019E-004	14.08	0.0199
B-Y2	1.019E-004	1	1.019E-004	14.08	0.0199
Residual	2.895E-005	4	7.238E-006	-	-
Cor Total	1.309E-004	5	-	-	-

Table VIII -Regression Statistics

Value of "Probability > F" and 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 8 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.

Conclusions

The experimental data compared with RSM model can be successfully relate 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 can be effectively used for predicting the complex formation along with the experimental results having more than 95% confidence level.

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