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Optimized Synthesis Conditions of Ionic Liquid-Silica Using Response Surface Methodology

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To develop the methodology of the surface coverage of ionic liquid -silica, conditions of the synthesis were optimized using the fractional factorial design with three-variables and three-levels by a response surface methodology computer program. Variables, such as the amount of silica (g), volume of silane (mL) and amount of imidizole (g), were investigated. The following optimum conditions were derived by response surface methodology: amount of silica = 20 g, volume of silane = 0.1 mL and amount of imidazole = 0.53 g. The theoretical surface coverage of ionic liuqid-silica (0.382) was obtained under the above conditions using the Design-Expert software.

Keywords: Response surface methodology, Ionic liquid-silica, Synthesis.

INTRODUCTION

Ionic liquids (ILs) are employed as a green reaction media and received a lot of attentions in the fields because they have attractive properties, such as low vapor pressure that does not volatilization under atmospheric pressure. In addition ionic liquids have good physical properties, such as melting point, viscosity, density and hydrophilicity/hydrophobicity. Ionic liquids can be synthesized easily by adjusting the combination of cations and anions to produce a so called "designer solvent"[1,2]. Therefore, separation, catalysis, synthesis, liquid chromatography and capillary electrophoresis have attracted increasing interest for ionic liquids[3]. General ionic liquid-based extraction technology has some disadvantages, such as a lower mass transfer rate and longer equilibrium time[4]. These problems can be overcome by immobilizing ionic liquids on different solid substrates. Surface coverage of ionic liquid-silica was relevant to the extraction and separation efficiency. Therefore, it is important to obtain a higher surface coverage in the synthesis process of ionic liquid-silica. A supported ionic liquid phase combines the advantages of ionic liquids with those of heterogeneous support materials. Some studies have successfully confined a range of ionic liquid phases to the surface of support materials and examined their potential catalytic applications. For analytical chemistry applications of a supported ionic liquid phase, ionic liquid-modified silica particles were used as a high performance liquid chromatography stationary phase to separate familiar organic compounds[5,6] and as a sorbent for the solid phase extraction of organic compounds[7,8]. Ionic liquid-modified silica particles, which consists of bulky organic cations (such as imidazolium) combined with inorganic or organic anions, has recently been developed as a new sorbent material. As ionic liquids are green, high-tech reaction media and show excellent chemical properties[9], they have attracted attention and been applied in a range of fields in analytical chemistry, such as sample preparation, organic synthesis, liquid-phase extraction and chromatographic separations[10,11]. Ionic liquid-modified silica has been used successfully in separation work owing to its characteristic cations and anions. On the other hand, there are few reports on optimizing the coverage rate using a mathematic methodology.

A statistical-based technique, commonly called response surface methodology (RSM), examines the relationships between several explanatory variables and one or more response variables and has been applied successfully to optimize the conditions[12,13]. Response surface methodology is a collection of mathematical and statistical techniques used to develop, improve and optimize processes and can be used to evaluate the relative significance of several affecting factors, even in the presence of complex interactions[14]. The response surface methodology has two kinds of typical design methods. Central composite response design (CCD) is for building a second order model for the response variable without needing to use a complete three-level factorial experiment[15]. Box-Behnken design (BBD) is used to calibrate full quadratic models. Box-Behnken design is rotatable and for a small number of factors (four or less), require fewer runs than central composite response design. By avoiding the corners of the design space, Box-

Behnken design allow experimenters to work around extreme factor combinations. However, extremes are then poorly estimated[16]. Fig. 1 shown cube for central composite response design and Box-Behnken design geometry model [a. central composite response design (CCD), b. Box-Behnken design (BBD)]. This study proposes an optimization approach provided by the Box-Behnken design, which is a response surface methodology that uses Design-Expert software (Version 7.0.0, Stat-Ease Inc., Minneapolis, USA).

This study examined the significant variables (amount of silica, volume of silane and amount of imidazole) to optimize the process for the synthesis of ionic liquid-silica using RSM employing a three-level, three-variable Box-Behnken design.

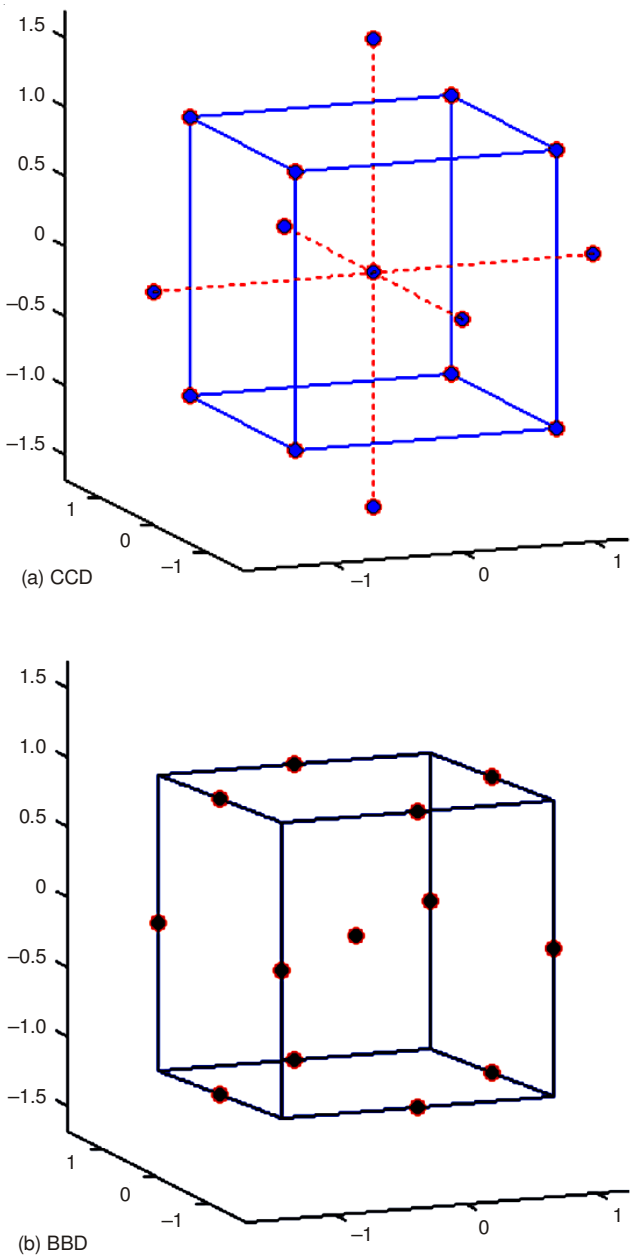

Fig. 1. Cube for central composite response design (CCD) and Box-Behnken design (BBD) geometry model (a. CCD, b. BBD).

EXPERIMENTAL

Silica, imidazole and (3-chloropropyl) trimethoxysilane obtained from Sigma-Aldrich (Milwaukee, WI, USA). Methanol, triethylamine and toluene were purchased from Duksan Pure Chemical Co., Ltd. (Ansan, Korea). All chemicals and reagents were of high performance liquid chromatography grade.

Synthesis of ionic liquid-silica and analysis: Different amount of silica and imidazole were added to 50 mL toluene, followed by different amount of (3-chloropropyl) trimethoxy-silane. The mixture of silica, imidazole and (3-chloropropyl) trimethoxy-silane was mixed in an agitator at the same condition such as 0.3 mL triethylamine as the catalyst in 80 °C for 8 h. The reactions were analyzed by the surface coverage of silica-ionic liquid, which was calculated using equation: $S = (m_1-m_0)/m_s$, where S is the surface coverage, m_1 is the weight of after the synthesis, m_0 is weight of before the synthesis and m_s is the weight of silica. Fourier transform infrared (FT-IR, Vertex 80 V, Bruker, Billerica, MA, USA) spectroscopy was performed over the range, 4000-400 cm^{-1}, at a scan rate of 20 scans min^{-1}. A KBr pellet was used for analysis. FT-IR spectroscopy is a powerful tool for providing conformational and structural information. The spectra of ionic liquid-modified silica exhibited an inconspicuous peak at 1575 cm^{-1} and the finger print region of the amide bands ranged from 1600 to 1500 cm^{-1}. This means some C-N groups had interacted with the commercial silica

Experimental design: 17- Run Box-Behnken design with Design-Expert (Stat-Ease, Inc., USA) software was used to optimize the ionic liquid-silica synthesis conditions. The surface coverage was selected as the response variable, whereas amounts of silica (X_1), (3-chloropropyl)trimethoxysilane (X_2) and imidazole (X_3) were selected as three independent variables. Table-1. shows the variables divided into three levels, coded as +1, 0 and -1 for high, intermediate and low values, respectively. To develop the regression equation, the relationship between the coded values and actual values was described using the following equation.

$$x_i = (X_i-X_0)/\Delta X,\ i = 1, 2, 3 \quad (1)$$

where x_i is the coded value of the independent variable, X_i is the actual value of the independent variable, X_0 is the actual value of the independent variable at the center point and ΔX is the step change in the independent variable. A polynomial model was used to correlate the relationship among the independent variables and response (surface coverage).

TABLE-1
INDEPENDENT VARIABLES AND THEIR LEVELS USED FOR BOX-BEHNKEN DESIGN

Variables	Level		
	-1	0	1
Amount of silica (X_1) (g)	1	10	20
Volume of silane (X_2) (mL)	0.1	5	10
Amount of imidazole (X_3) (g)	0.01	0.5	1

$$Y = A_0 + \sum_{i=1}^{3} A_i X_i + \sum_{i=1}^{3} A_{ii} X_i^2 + \sum_{i=1}^{2} \sum_{j=i+1}^{3} A_{ij} X_i X_j \quad (2)$$

where Y is the response (surface coverage), A_0 is a constant, A_i is a linear coefficient, A_{ii} is a quadratic coefficient and A_{ij} is an interactive coefficient. X_i and X_j are uncoded independent variables. The equation examined the effects of each independent variable on the response.

RESULTS AND DISCUSSION

First time experimental was conducted an experiment under low independent variable level. The result, the calculated value and experimental value was surface coverage is low value. Therefore, a second experiment was used to extend the range of independent variables.

Model fitting and statistical analysis: The optimal conditions of the important factors were determined using a 17-run Box-Behnken design. The Box-Behnken design was used to calibrate the full quadratic models. Table-2. presents the experimental data for ionic liquid-silica synthesis. The predicted responses were obtained from a model fitting technique using the software design expert. The predictive equation was obtained by fitting the experimental data to the Box-Behnken design model in eqn. (3). The quadratic polynomial is given as follows:

$$Y = 0.1 - 0.15X_1 + 0.016X_2 - 0.012X_3 - 0.17X_1X_2 + 0.028X_1X_3 + 3.41E^{-0.03}X_2X_3 + 0.19X_1^2 + 0.079X_2^2 - 0.12X_3^2 \quad (3)$$

The importance of each coefficient was confirmed using the F-value and p value, which are listed in Table-3. The p-value is the probability of obtaining a test statistic at least as extreme as the one that was actually observed, assuming that the null hypothesis was true. One often "rejects the null hypothesis" when the p-value is less than 0.05. The result is said to be statistically significant when the null hypothesis is rejected[17]. The model p-value was 0.0001, indicating that the model terms were significant. The model F-value of 143.22 suggests that the model is significant. The probability of a "Model F-value" of 143.22 occurring due to noise was only 0.01 %. Table-4. lists the coefficient of determination (R^2), adjusted coefficient of determination (R^2_{Adj}) and coefficient of variation (CV). The model showed a good fit with the experimental data because the coefficient of determination R^2 was 0.995 and the adjusted coefficient of determination R^2_{Adj} was 0.988. This suggests that the accuracy and general availability of the polynomial model were adequate and a R^2_{Pred} of 0.914 showed reasonable agreement with R^2_{Adj}. The "Adeq. Precision" measured the signal to noise ratio and a ratio of greater than 4 is normally desirable. The "Adeq. Precision" of 44.440 indicated that this model could be used to navigate the design space.

TABLE-3
ANALYSIS OF VARIANCE OF THE EXPERIMENTAL RESULTS OF THE BOX-BEHNKEN DESIGN

Source	DF	F Value	p-value Prob > F
Model	9	143.22	< 0.0001
X_1	1	418.75	< 0.0001
X_2	1	5.18	0.0571
X_3	1	2.64	0.1480
X_1X_2	1	276.03	< 0.0001
X_1X_3	1	7.66	0.0278
X_2X_3	1	0.11	0.7460
X_1^2	1	388.75	< 0.0001
X_2^2	1	63.34	< 0.0001
X_3^2	1	142.39	< 0.0001
Residual	7	-	-
Lack of fit	3	1.29E + 005	< 0.0001
Pure error	4	-	-
Correlation total	16	-	-

TABLE-4
ANALYSIS OF VARIANCE FOR THE FITTED QUADRATIC POLYNOMIAL MODEL OF SYNTHESIS OF IONIC LIQUID-SILICA

Item	Std. dev.	C.V. (%)	R^2	R^2_{Adj}	R^2_{Pred}	Adeq. precision
Value	0.020	11.470	0.995	0.988	0.914	44.440

Optimization of the synthesis conditions: The optimal conditions for the synthesis of ionic liquid-silica were predicted using the optimization function of Design Expert Software. The 2D contour plot and 3D response surface plots are provided as graphical representations of the regression equation (Figs. 2-4). Each contour curve represents an infinitive number of combinations of two test variables with the other factors fixed at the zero level. Fig. 2 shows the effects of the amounts of silica, amounts of silane and their reciprocal interactions on the surface coverage. The surface coverage increased with decreasing amounts of silica and increasing silane volume up to 1 g and 10 mL, respectively. Fig. 3 shows the effect of the

TABLE-2
BOX-BEHNKEN EXPERIMENTAL DESIGN WITH THREE INDEPENDENT VARIABLES

Run	Coded variable levels			Parameter of surface coverage (g/g)	
	X_1	X_2	X_3	Experimental values	Calculation values
1	-1	-1	0	0.328	0.321
2	1	-1	0	0.364	0.373
3	-1	1	0	0.725	0.729
4	1	1	0	0.089	0.093
5	-1	0	-1	0.375	0.379
6	1	0	-1	0.033	0.029
7	-1	0	1	0.271	0.277
8	1	0	1	0.041	0.043
9	0	-1	-1	0.065	0.052
10	0	1	-1	0.062	0.115
11	0	-1	1	0.059	0.007
12	0	1	1	0.070	0.072
13	0	0	0	0.103	0.103
14	0	0	0	0.103	0.103
15	0	0	0	0.103	0.103
16	0	0	0	0.103	0.103
17	0	0	0	0.103	0.103

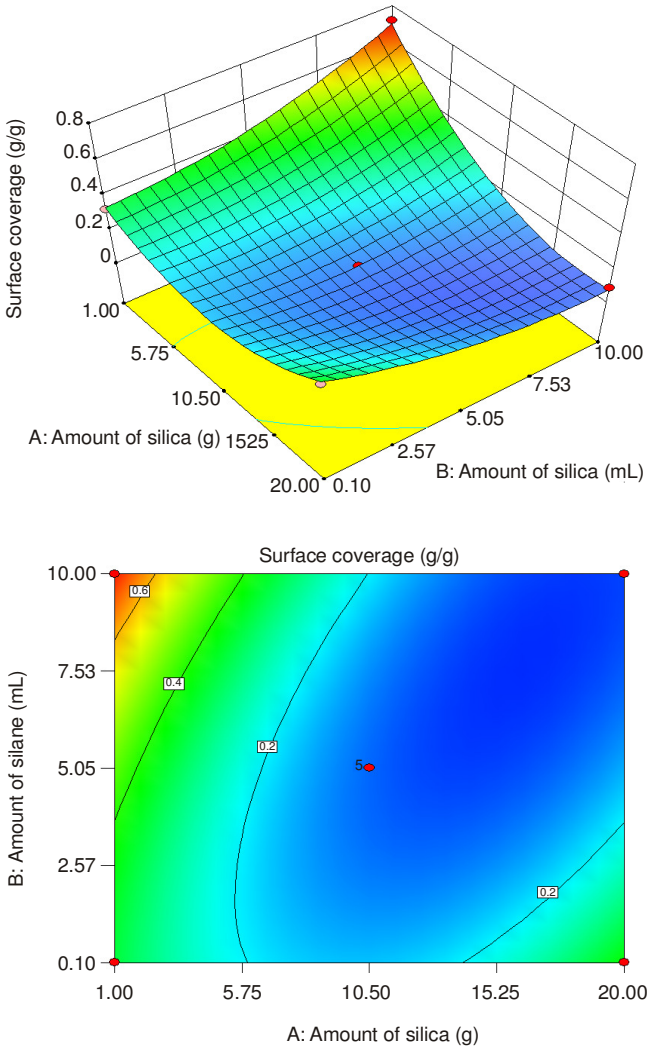

Fig. 2. Imidazole when the zero level, effect of the amount of silica, silane and their reciprocal interaction on surface coverage (a. 3D response surface; b. 2D contour plots)

amounts of silica and amounts of imidazole and their reciprocal interaction on the surface coverage. The surface coverage was lower at high amounts of silica and low or high amounts of

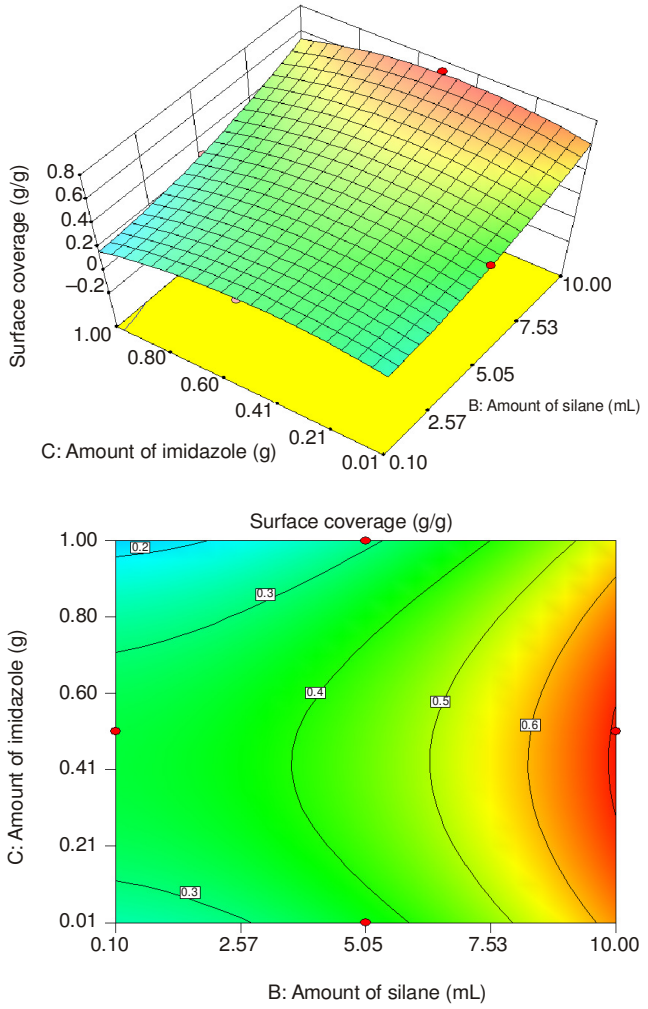

Fig. 4. Silica when the zero level, effect of the amount of silane, IL and their reciprocal interaction on the surface coverage (a. 3D response surface; b. 2D contour plots)

imidazole. A reaction with a low amount of silica and imidazole (0.4-0.6 g) produced maximal surface coverage. Fig. 4 shows the effect of the amounts of silica, amounts of imidazole and their reciprocal interaction on the surface coverage. The surface coverage was lower at low amounts of silane and low or high

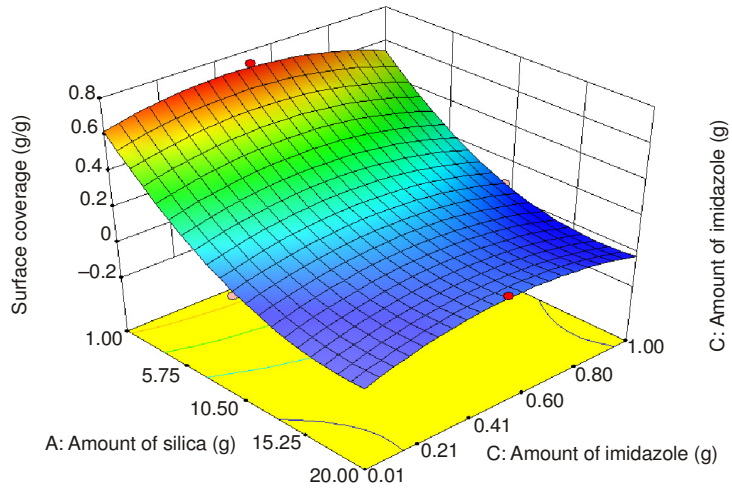

Fig. 3. Silane when the zero level, effect of the amount of silica, imidazole and their reciprocal interaction on surface coverage (a. 3D response surface; b. 2D contour plots

amounts of imidazole. A reaction with high amounts of silane and amounts of imidazole (0.4-0.6 g) showed the maximum surface coverage.

The optimum extraction conditions (X_1 = 20 g, X_2 = 0.1 mL and X_3 = 0.53 g) for the ionic liquid-silica surface coverage were estimated using the model equation by solving the regression equation and analyzing the response surface contour plot. The theoretical surface coverage of ionic liquid-silica (0.382 mg g^{-1}) was obtained under the above conditions using Design-Expert software.

Conclusion

A comparison of the predicted and experimental values revealed good correspondence, suggesting that the empirical models derived from response surface methodology can be used to adequately describe the relationship between the factors and response in ionic liquid-silica synthesis. These models can then be used to predict the surface coverage under any given conditions within the experimental range. The optimum synthesis of ionic liquid-silica can be predicted successfully using response surface methodology.

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