Available online at www.sciencedirect.com

SCIENCE DIRECT

Journal of Solid State Chemistry 177 (2004) 675–680

JOURNAL OF
SOLID STATE
CHEMISTRY

http://elsevier.com/locate/jssc

Full factorial design applied to intercalation of amines in lamellar titanium phenylphosphonate and titanium phenylarsonate

Vanusa S. O. Ruiz, Silvio L. P. Dias, Yoshitaka Gushikem, Roy E. Bruns, and Claudio Airoldi*

Instituto de Química, Universidade Estadual de Campinas, Caixa Postal 6154, 13084-901 Campinas, São Paulo, Brazil

Received 3 June 2003; received in revised form 7 August 2003; accepted 19 August 2003

Abstract

The intercalation of amines into titanium phenylphosphonate $M(O_3PC_6H_5)_2$ and titanium phenylarsonate $M(O_3AsC_6H_5)_2$ was investigated through batch and back-titration processes. Amine insertion in both layered lamellar inorganic matrices, measured by the number of moles of intercalated agent, was optimized using a complete factorial design based on two levels and four factors. The effects of solvent, ethanol and acetonitrile, neutral organic base, ethyl and propylamines, $H_3C(CH_2)_nNH_2$ ($n = 1, 2$), and material mass, 30 and 40 mg, on amine insertion in both lamellar inorganic matrices was optimized using a full factorial design. Important positive effect values, 0.40×10^{-3} and $0.69 \times 10^{-3}\,\mathrm{mol\,g^{-1}}$ were observed for inorganic material and solvent whereas a negative effect, $-0.33 \times 10^{-3}\,\mathrm{mol\,g^{-1}}$ was observed for material mass. Two significant but less important binary interactions were also observed. The use of either ethyl or propylamine does not appear to affect the quantity of amine insertion. Recommended experimental conditions for maximum amine insertion obtained from this factorial design are 30 mg of titanium phenylarsonate in acetonitrile solvent using either of the studied amines.

Keywords: Phenylphosphonate; Phenylarsonate; Titanium; Intercalation; Factorial design

1. Introduction

The chemistry of intercalation is a research area that has been widely investigated and plays a very important part in applications in many academic and technological fields, such as those related to catalysis, ion-exchange processes, magnetic determinations and supports for catalytic methods [1–6].

A great variety of natural and synthetic inorganic compounds are susceptible to intercalation processes, whose final properties are connected to their respective structures, specially the distribution of the inorganic backbone in a lamellar arrangement. One of the most important inherent properties of these types of layered materials is concerned with the fact that they can expand the interlamellar space, when exposed to guest species [1,7,8].

The crystalline layered compounds exhibit some attractive properties such as, high thermal stability, resistance to oxidation, high selectivity to a series of ions and molecules, and convenience for chemical modifications [7]. In this class of materials, natural clays [9], phyllosilicates [10], double hydroxides [7], silicic crystalline acids [8], polymeric silicates [11], transition metals oxides [12] metallic phosphates and phosphonates [1–3] are included, all of which can accommodate intercalating agents in free interlamellar space.

The inorganic lamellar compounds of tetravalent metals are the most commonly and extensively explored, constituting a well-studied group of compounds of general formula $M(HXO_4)_2 \cdot H_2O$ (M = Zr, Ti, Ge, Sn, etc. and X = P or As). Therefore, similar series of these kinds of compounds based mainly on organophosphonic and less on organoarsonic acids, with titanium and zirconium elements can be synthesized. In all cases, neutral polar species like alkyl or arylamines can be inserted inside these lamellar structures, which results in similar inorganic matrices compared to those of the original host, although they have distinct physical–chemical properties [13–15].

---

*Corresponding author. Fax: +55-19-3788-3023.
E-mail address: airoldi@iqm.unicamp.br (C. Airoldi).

0022-4596/$ - see front matter © 2003 Elsevier Inc. All rights reserved.
doi:10.1016/j.jssc.2003.08.016

Several factors can influence the intercalation of organic species in the interlamellar space such as the specific type of matrix, solvent, intercalating organic group and the mass of the sample. The investigation of these factors permits recognition of their influence level on the insertion process of the guest species. These investigations can be carried out by classical methods, varying each factor separately. However, the experimental factorial design investigations present several advantages over such univariate methods [16,17].

Factors are varied simultaneously rather than one-at-a-time permitting observation of synergic and antagonistic interactions involving the factors. Univariate methods are incapable of measuring these interactions and for this reason are not effective optimization techniques. Furthermore factorial designs permit system optimization by performing a minimum number of experiments.

The aim of this investigation is to use a 2^4 full factorial design to evaluate the effects of titanium phenylphosphonate or titanium phenylarsonate material type, ethanol or acetonitrile solvent, ethylamine or propylamine neutral organic bases and 30 or 40 mg sample mass, on the number of moles of organic base intercalated in the inorganic matrix. Also possible interactive synergistic or antagonistic effects involving these factors will be measured permitting a successful optimization of the insertion process.

2. Experimental

All chemical are at least of analytical reagent grade. Solutions were prepared with deionized water. Titanium chloride (Aldrich) presented 10% of $TiCl_3$ in HCl solution and the *n*-alkylamines $[CH_3(CH_2)_nNH_2]$ (Fluka Chemika), ethylamine and propylamine, were used without any purification. Phenylphosphonic $[(C_6H_5PO(OH)_2]$ (Aldrich), 98% and phenylarsonic $[(C_6H_5AsO_3H_2]$ (Aldrich) 97% acids were used in both synthetic procedures.

2.1. Synthesis

Titanium phenylphosphonate and titanium phenylarsonate were synthesized as previously described [18]. Briefly, 60.0 cm^3 of 1.0 $mol\,dm^{-3}$ acid solutions were mixed with 25.0 cm^3 of 0.50 $mol\,dm^{-3}$ titanium chloride solution. The reaction was maintained at 353 K with stirring for 7 days and oxidation was favored through periodic flow of gaseous oxygen at around 2.08 $cm^3\,s^{-1}$ into the reaction mixture. The solid formed was washed several times with distilled water until pH 4 and the supernatant was eliminated by centrifugation at 3000 rpm, for 10 min. Then, the solid was dried for 2 days at 323 K and maintained in a tightly closed polyethylene flask.

2.2. Intercalation

Amine intercalation into titanium phenylphosphonate and titanium phenylarsonate was carried out using a process described previously [19,20]. Ethyl and propylamine solutions were prepared in ethanol 0.3938 and 0.3787 $mol\,dm^{-3}$ and acetonitrile 0.3837 and 0.4796 $mol\,dm^{-3}$, respectively, and the solutions were standardized by hydrochloric acid titration, using a mixture of bromocresol green and methyl red in a 5:1 proportion as indicator. A series of samples with 30 or 40 mg of each matrix containing 6.0 cm^3 was suspended in amine solutions in order to carry out the factorial design. For each isotherm, a series of flasks containing the suspensions received additions of 30 μL of the amine solutions, which were continuously stirred in an orbital mechanical apparatus thermostated at 298 ± 1 K for 24 h. After this time the inorganic matrices were centrifuged at 3000 rpm for 10 min and the liquid was back-titrated. Then, the number of moles of amine intercalated was obtained by titrating aliquots of the filtrated with standardized hydrochloric acid solution. The number of amine molecules intercalated increased with the concentration of the supernatant until at the plateau of the total saturation of the layered structure was reached, to give experimental optimization to establish the best condition to apply for calorimetric procedure. From this operation, the number of moles of organic base inserted per gram of inorganic matrix, n_f, can be calculated by the expression [19–21]:

$$n_f = (n_i - n_s)/m, \tag{1}$$

where n_i is the number of moles of organic base added, n_s number of moles of organic base at equilibrium and m is the mass of the inorganic matrix.

2.3. Full factorial designs

One of the simplest types of factorial designs used in chemistry is the one having two levels. The design determines which factors have important effects on a response as well as how the effect of one factor varies with the level of the other factors. Effects are differential quantities expressing how a response changes as the levels of one or more factors are changed. The determinations of factor interactions can be important for successful system optimization. In this investigation of amine intercalation, the number of moles of inserted amine in the titanium phenylphosphonate and titanium phenylarsonate inorganic matrices can depend on the type of matrix material, the amine type, the solvent and the amount of matrix mass.

Table 1
2^4factorial design for the number of moles (N_f) intercalated (mol g^{-1}) in the matrix materials

Experiment	Sequence of operation	1	2	3	4	$N_f \times 10^{-3}$
1	1	—	—	—	—	1.55 ± 0.01
2	9	+	—	—	—	2.02 ± 0.02
3	5	—	+	—	—	2.39 ± 0.01
4	13	+	+	—	—	2.58 ± 0.01
5	3	—	—	+	—	1.41 ± 0.01
6	11	+	—	+	—	2.15 ± 0.01
7	7	—	+	+	—	2.24 ± 0.01
8	15	+	+	+	—	2.75 ± 0.01
9	2	—	—	—	+	1.23 ± 0.01
10	10	+	—	—	+	1.68 ± 0.03
11	6	—	+	—	+	2.12 ± 0.02
12	14	+	+	—	+	2.07 ± 0.01
13	4	—	—	+	+	1.22 ± 0.03
14	12	+	—	+	+	1.75 ± 0.01
15	8	—	+	+	+	2.01 ± 0.01
16	16	+	+	+	+	2.39 ± 0.01
1—Type of material	$Ti(O_3PC_6H_5)_2$	$Ti(O_3AsC_6H_5)_2$				
2—Solvent	H_3CCH_2OH	H_3CCN				
3—Neutral organic base	$H_3CCH_2NH_2$	$H_3C(CH_2)_2NH_2$				
4—Mass of sample (mg)	30	40				

The effects of these factors and their interactions are measured by performing 16 experiments forming the 2^4 full factorial designs given in Table 1. For convenience, each factor level is codified as -1(low) or $+1$(high) and the effect values are calculated using the equation [16,17]:

$$Ef_i = \bar{R}_i^{(+)} - \bar{R}_i^{(-)},$$

where $\bar{R}_i^{(+)}$ and $\bar{R}_i^{(-)}$ are the averages of results when the ith factor is at its high (+) or low (−) level independent of the signs of the other effects. Eight experimental values make up each average because each column in Table 1 has eight positive and eight negative signs. The 16 experiments were performed in random order. This complete factorial design is particularly efficient for the evaluation of the main effects of each factor and of the interactions of two or more factors on the number of moles of inserted base. Univariate methods are not able to measure these interactive effects [16]. The definitions of the factors and levels used in the full factorial design and the number of moles of inserted amine for each experiment are also presented in Table 1. These listed numbers represent the mean value for three independent determinations.

3. Results and discussion

The present study considers the inorganic titanium phenylphosphonate and titanium phenylarsonate, $M(O_3XC_6H_5)_2$, (M=Ti, X=P, As) matrices, because these materials present similar lamellar structures, differing only in the central P or As atoms. The choice of ethyl and propylamines, $H_3C(CH_2)_nNH_2$ (n=1, 2), neutral organic bases is due mainly to the fact that their structures differ slightly in carbon chain size, causing only a small change in lamellar space in both inorganic matrices. Thus, an evaluation of the capacity of intercalation of these two inorganic supports can be made. The choice of the solvents, ethanol or acetonitrile and the sample mass, 30 and 40 mg, is due mainly to previous investigations, which suggested these levels as the most appropriate conditions for further study [22–24].

Effect values calculated from the experimental results in Table 1 using Eq. (1) are presented in Table 2. The most important effects (largest absolute magnitudes) are the type of inorganic material, the solvent and the material mass. All the interaction effects and the main effect of organic base have smaller absolute magnitudes than these main effects.

The main effect values can be better understood on examining more closely the results in Table 1. On comparing pairs of experiments that differ only in the sign of factor 1, for example, run 1 with 2, 3 with 4 etc., it can be observed that, for almost all pairs, the largest result occurs when factor 1 is at its high level. The only exception is the pair of runs 11 and 12 where the experimental results are about the same, 2.12×10^{-3} and 2.07×10^{-3} moles, respectively. This indicates that on changing from phenylphosphonate to phenylarsonate an increase in the number of intercalated moles occurred, i.e., this factor has a positive effect.

Comparing pairs of runs that differ only in the sign of factor 2, runs 1 and 3, 2 and 4, etc., an even clearer trend is observed. Independent of the levels of the other

Table 2
Principal and interaction effect values for the 2^4 factorial design[a]

Principal effect	10^{-3} (mol g^{-1})
1 (Type of material)	0.40 ± 0.04
2 (Solvent)	0.69 ± 0.04
3 (Neutral organic base)	0.035 ± 0.04
4 (Mass of material)	-0.33 ± 0.04
Interaction of two factors	
12	-0.15 ± 0.04
13	0.14 ± 0.04
14	-0.075 ± 0.04
23	0.043 ± 0.04
24	-0.015 ± 0.04
34	0.033 ± 0.04
Interaction of three factors	
123	0.050 ± 0.04
124	-0.018 ± 0.04
134	-0.010 ± 0.04
234	0.015 ± 0.04
Interaction of four factors	
1234	0.038 ± 0.04

[a] 95% confidence interval of ± 0.081 calculated for these effects.

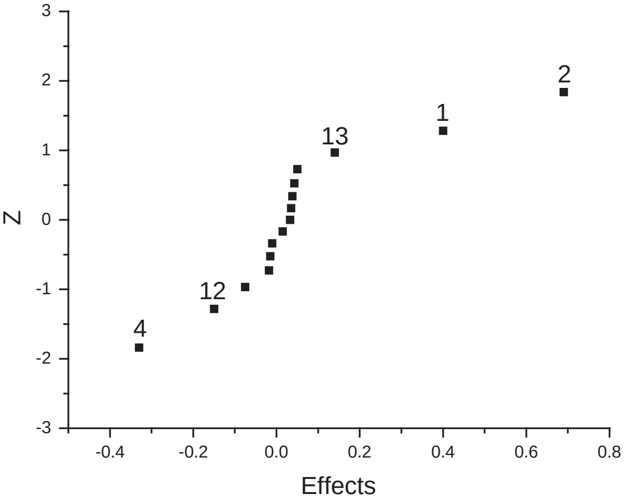

Fig. 1. Cumulative probability graph for the effect values of the 2^4 factorial design in Table 2.

factors the result is always larger when acetonitrile is used as a solvent. An opposite trend is seen for the material mass. Comparing results for runs 1 and 9, 2 and 10, etc., a smaller number of intercalated moles is found when 40 mg of material are used instead of 30 mg. Hence material mass has a negative effect. On the other hand, it is not possible to see such a trend for the neutral organic base factor. Comparisons made between the results of runs 1 and 5, 2 and 6, etc., show that the response decreases for four pairs and increases for the other four suggesting random variations on changing from ethyl to propylamine while the other factors are maintained at constant levels. This behavior indicates the absence of a statistically significant main effect for this factor. In summary, there appears to be three important main effects, positive ones for the type of inorganic material and solvent, and a negative one for material mass.

The statistical significance of all these effects can be determined by plotting the effect values on a cumulative probability graph [16,17]. The effect values are graphed on the abscissa whereas expected cumulative probability values for a normal distribution are graphed on the ordinate. The cumulative probability graph for the effect values in Table 2 are shown in Fig. 1. Points corresponding to a normal distribution are expected to be located on a vertical line centered about the origin. The effects these points represent are not significant and only provide estimates of effect errors. Five points are clearly removed from the line in the center of the graph and their effect values are statistically significant. Besides the main effects of inorganic material, solvent and material mass, which correspond to the three points farthest from the line, the other two represent two factor interaction effects between inorganic material and solvent (-0.15×10^{-3} moles) and inorganic material and neutral organic base (0.14×10^{-3} moles). These effects appear to be statistically significant but are not as important as the main effects that have larger absolute magnitudes.

The mean sum of squares of the effect values that are considered to belong to the normal distribution provide an estimate of the effect variance, $V(\mathrm{Ef}_i) = 0.001329$. Its square root corresponds to an estimated 0.0365 effect error and a 95% confidence interval of $\pm(0.0365)(2.228) = \pm 0.0813$ where Student's t-distribution value for ten degrees of freedom is 2.228. The absolute values of the two interaction effects are larger than 0.0813 confirming that they are indeed statistically significant.

The largest absolute magnitude in the Table 2 occurs for the main effect of the solvent. A change in solvent from ethanol to acetonitrile resulted in an increase in the degree of intercalation of 0.69×10^{-3} mol g^{-1}. This increase had previously been observed in non-aqueous solvents [25] so it is expected that the solvent molecule has an important role in the replacement process. In this case, the characteristic of the molecules involved in the interactive reaction of the Lewis base center with the active sites of the inorganic matrix, should be considered. Therefore, a reasonable explanation for this behavior can be obtained by comparing the individual donor numbers [26] of ethanol and acetonitrile, which are 20 and 14, respectively. Thus, acetonitrile forms the weakest bond with the inorganic matrix, enabling its replacement during the intercalation process. Consequently, base insertion is favored, reflecting an increased response for acetonitrile in comparison with ethanol.

The change of the inorganic support from titanium phenylphosphonate to titanium phenylarsonate causes an increase in the intercalation degree by $0.40 \times 10^{-3}\,\text{mol}\,\text{g}^{-1}$. A speculative explanation for this fact could be also associated with the possible additional Lewis acid centers located on the arsenic atom. Based on this proposal, in principle, an additional amine–arsenic bond can be formed, by increasing the number of moles of attached amine beyond the maximum permitted for a Lewis acid center, represented by identical titanium atoms for these compounds.

The absence of an important main effect for the neutral organic base factor can be explained by considering the $\text{p}K_\text{a}$ values 10.70 and 10.60 for ethyl and propylamine, respectively [27]. Changes in the length or extent of branching of an aliphatic hydrocarbon usually have small effects on the $\text{p}K_\text{a}$ values of the corresponding amine or carboxylic acid in aqueous solution. The inductive effect of an alkyl group is small and falls off rapidly with distance from the reaction center, so that only atoms that are near neighbors to the acidic or basic centers exert a significant effect on observed $\text{p}K_\text{a}$ values. Thus, since the $\text{p}K_\text{a}$ values of aliphatic amines are not appreciably changed if ethyl groups replace larger propyl groups one does not expect a large organic base effect for this factorial design.

It is indeed intriguing that the number of intercalated moles of base decreases as the sample mass used increases. One could expect the opposite behavior and a positive material mass effect in Table 2. However, this effect is both significant and important and does not depend on the levels of the other factors because no interaction effect involving factor 4 is significant.

The analysis of the response values is most convenient by using the factorial diagram in Fig. 2. It allows confirmation of the simple behavior for the values of the number of moles of intercalated agent reported earlier in this investigation. The positive $0.69\,\text{mol}\,\text{g}^{-1}$ solvent effect value appeared because all the number of mole values for the main effect of the ethanol solvent (left side of the cube) are $0.5–0.85\,\text{mol}\,\text{g}^{-1}$ smaller than the values corresponding to the acetonitrile solvent (right side of the cube). Similar arguments using the front and back faces for the amounts of inorganic support mass, and the upper and lower faces for the material type, titanium phenylphosphonate and titanium phenylarsonate, can be used to better understand the physical interpretation of the main effects for the number of moles of intercalated agent. The recommended conditions for obtaining the largest number of moles of intercalated agent from this factorial study, are given by those of the + +-run (titanium phenylarsonate, acetonitrile, 30 mg). The levels for this maximum value are consistent with the effect values in Table 2, positive ones for material type and solvent and a negative one for material weight.

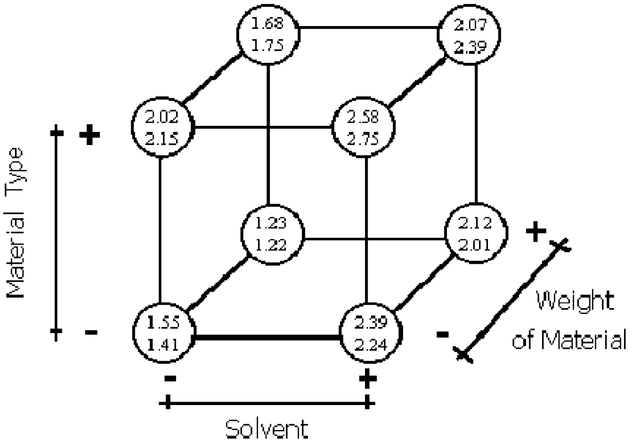

Fig. 2. Cubic representation of the factorial design results of the intercalation of amines in titanium phenylphosphonate and phenylarsenate, (intercalation values $\times 10^{-3}\,\text{mol}\,\text{g}^{-1}$).

4. Conclusion

This investigation shows that the factorial design provides an efficient way to plan experiments involving the insertion of neutral organic bases in a layered lamellar inorganic support, and thus optimize the intercalation process of these amines. The full 2^4 factorial design used allowed the simultaneous investigation of four factors executing only 16 experiments. The values of the effects showed that there are three significant main effects, material type, solvent and material mass, besides two smaller binary interaction effects, inorganic material–solvent and inorganic material–organic base. These two interactions present little influence on the system. Based on the 2^4 factorial results one can assume that the neutral organic base factor is inert. The experimental observations and the data analysis indicate that the optimized conditions for this system correspond to the run with 30 mg of titanium phenylarsonate in acetonitrile solvent.

Acknowledgments

The authors are indebted to FAPESP for financial support and fellowship to VSOR, and CAPES/PICDT for a fellowship to SLPD.

References

[1] G. Alberti, F. Marmottini, S. Cavalaglio, D. Severi, Langmuir 16 (2000) 4165.
[2] J.M. Kevin, J.S. Philip, A. Clearfield, Inorg. Chim. Acta 155 (1989) 7.
[3] C. Guang, M.L. Vincent, N.Y. Leonard, Chem. Mater. 5 (1993) 1000.

[4] G. Cao, V.M. Lynch, J.S. Swinneaand, T.E. Mallouk, Inorg. Chem. 29 (1990) 2112.

[5] F. Fredoueil, D. Massiot, P. Janvier, F. Gingl, M.B. Doeuff, M. Evain, A. Clearfield, B. Bujoli, Inorg. Chem. 38 (1999) 1831.

[6] G. Cao, T.E. Mallouk, Inorg. Chem. 30 (1991) 1434.

[7] V. Prevot, C. Forano, J.P. Besse, J. Mater. Chem. 9 (1999) 155.

[8] K. Endo, Y. Sugahara, K. Kuroda, Bull. Chem. Soc. Jpn. 67 (1994) 3352.

[9] V. Kuyendall, J.K. Thomas, Langmuir 6 (1990) 1346.

[10] M.G. Fonseca, C. Airoldi, J. Mater. Chem. 9 (1999) 1375.

[11] T. Yanagisawa, K. Kuroda, C. Kato, Bull. Chem. Soc. Jpn. 61 (1998) 3743.

[12] Q. Feng, H. Kanoh, K. Ooi, J. Mater. Chem. 9 (1999) 319.

[13] P.O. Pastor, P.M. Torres, E.R. Castellon, A. Lopez, J. Chem. Mater. 8 (1996) 1758.

[14] Z. Wang, T. Lan, T. Pinnavaia, J. Chem. Mater. 8 (1996) 2200.

[15] E.R. Hitzky, J.M. Rojo, Nature 287 (1980) 28.

[16] G.P.G. Box, W.G. Hunter, S. Hunter, Statistics for Experimenters: An Introduction for Design, Data Analysis and Model Building, Wiley, New York, 1978.

[17] B.B. Neto, I.S. Scarmínio, R.E. Bruns, Como fazer experimentos: Pesquisa e Desenvolvimento na Ciência e na indústria, Ed. Unicamp, 2001.

[18] M.A.V. García, E. Jaimez, A. Bortun, J.R. García, J. Rodrígues, J. Porous Mater. 2 (1995) 85.

[19] C. Airoldi, M.R.M.C. Santos, J. Mater. Chem. 4 (1994) 1479.

[20] C. Airoldi, E.F.C. Alcântara, Colloids Surf. 39 (1989) 291.

[21] J.C. Moreira, Y. Gushikem, Anal. Chim. Acta. 176 (1985) 263.

[22] J.G.P. Espínola, J.M.P. Freitas, S.F. Oliveira, C. Airoldi, Colloids Surf. 87 (1994) 33.

[23] J.G.P. Espínola, C. Airoldi, Y. Gushikem, Colloids Surf. 17 (1986) 317.

[24] C. Airoldi, A.R. Cestari, J. Braz. Chem. Soc. 6 (1995) 291.

[25] C. Airoldi, S.F. Oliveira, Struct. Chem. 2 (1990) 41.

[26] V. Gutmann, The Donor–Acceptor Approach to Molecular Interactions, Plenum, London, 1978.

[27] D.D. Perrin, B. Dempsey, P.E. Sergeant, pK_a Prediction for Organic Acids and Bases, Chapman and Hall, London, 1981.